



TITLE:

Technological Development of an Effective Recycling System for Fly Ash from Municipal Solid Waste Incinerator to be Raw Material in Cement Industry( Dissertation\_全文)

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CITATION:

Zhu, Fenfen. Technological Development of an Effective Recycling System for Fly Ash from Municipal Solid Waste Incinerator to be Raw Material in Cement Industry. 京都大学, 2008, 博士(工学)

ISSUE DATE:

2008-09-24

URL:

<https://doi.org/10.14989/doctor.k14148>

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**FENFEN ZHU**



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**August 2008**

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# 1 INTRODUCTION

## 1.1 Background

Since the book, “Silent Spring”<sup>1</sup>, was published in 1962, it was like a big bomb blasted and people began to concern more about the environmental problems. Though we had done something since long before<sup>2</sup>, it was rough, unsafe and not effective enough<sup>2</sup>, since the negative impact on environment resulting from the development of our society is not easily to be repaired and the our action or knowledge to protect environment is not comprehensive<sup>3-5</sup>. And now we are facing more and more serious environment problems, which will in the end be the crisis for the existence of our own, human beings, such as global warming<sup>6, 7</sup>, serious desertification<sup>8, 9</sup>, energy and resources crisis. On the other aspects, we studied the feedback effect of influenced environment on human beings<sup>10-13</sup>. That is, human beings should develop harmoniously together with our environment. By this we developed the concepts of “Reduce, Reuse, Recycle” (3R)<sup>14, 15</sup>, sustainable development<sup>16-19</sup>, harmony society<sup>20</sup> and so on. We took and are taking actions to fulfill those concepts, which simultaneously modify our life styles, economy style and so on<sup>21-24</sup>.

As one of the most important parts of environment, municipal solid waste also needs to be set under environmentally and scientifically integrated management<sup>2</sup>. While, the integrated management of municipal solid waste includes many aspects<sup>2</sup>, here I would like to light on the special treatment technology —— incineration.

Incineration is a waste treatment technology that involves the combustion of organic materials and/ or substances. It is the conversion of solid wastes into gaseous, liquid, and solid conversion products, with the concurrent or subsequent release of heat energy<sup>2, 25</sup>. As one of the traditional technology, incineration is widely adopted in Japan and some European countries to treat municipal solid waste (MSW)<sup>26, 27</sup>. Figure 1.1 shows the amount of municipal solid waste treated in Japan from year 1996 to year 2005. From Figure 1.1 it can be seen that in Japan more than 75% MSW was treated by incineration. Not only in developed countries, but also in some big cities of several developing countries such as China, incinerators are also gradually being built.<sup>28, 29</sup>



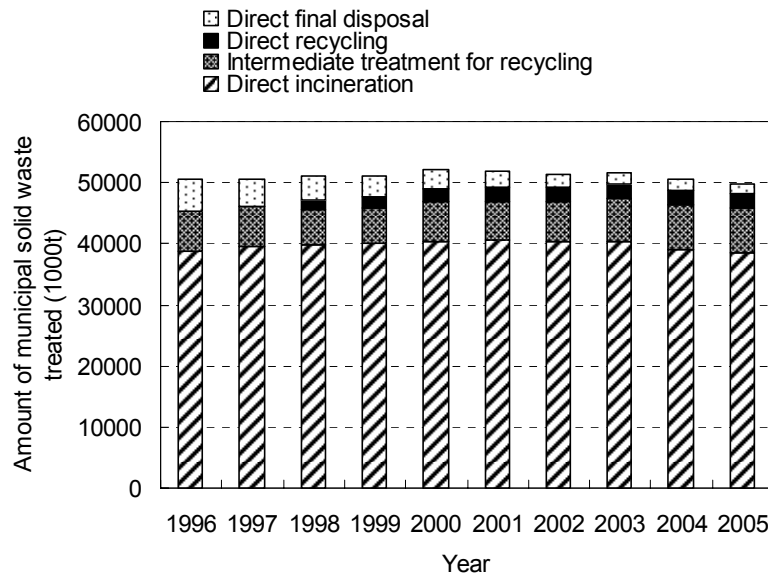


Figure 1.1 Amount of municipal solid waste treated in Japan (1996-2005)

Incineration has many advantages. First, it can effectively reduce the volume of the waste and the volume reduction rate can reach even more than 90%. Second, it occupies much less area than landfill and compost, which is very significant to the narrow place. Third, I can recover heat produced during incineration to generate electricity or to get hot water.

However, everything has two aspects. There are disadvantages. High cost is one of the main factors to prevent incineration from prevailing in developing countries. The World Bank estimates that the cost of incineration is “an order of magnitude greater than” direct landfilling<sup>30</sup>. In spite of the high cost, there is second pollution: discharged gas and bottom ash. Except the original particles in the discharged gas, in order to neutralize the acid compound in the discharged gas, we have to inject alkaline reagent, and we have to deal with the byproducts named fly ash produced through discharged gas treatment to protect air environment and another main byproduct is bottom ash, which remains at the bottom of incinerator as a direct incineration residue. In the discharged gas, fly ashes and bottom ashes, there are famous hazardous compounds——dioxins<sup>31</sup>. Heavy metals such as Hg in discharged gas, and Cr and Pb in fly ash and bottom ash are also highly concerned materials<sup>32,33</sup>. In addition to them, incineration is the considerable source of the carbon dioxide gas contributing to global warming<sup>34-36</sup>, and though there are instruments improvement or energy transform or utilization, the efficiency is not high enough at present<sup>34-36</sup>.

However, considering the current situation of Japan, the dominant position of

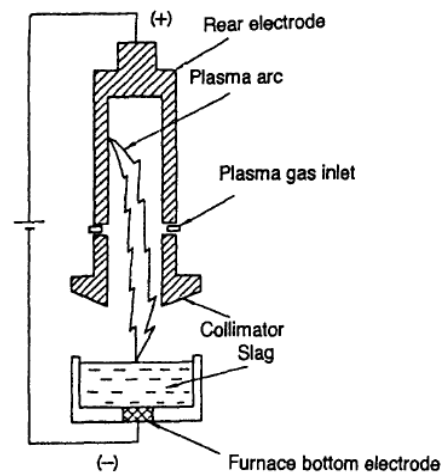
incineration in municipal solid waste management will not change in recent years. So how to reduce the negative effect of incineration to make it more environmentally friendly is an urgent task for environment scientists. My research focuses on the fly ash including the raw fly ash from the boiler and the residue from the air pollution control system.

## **1.2 Existing Intermediate Treatment for Fly Ash from MSW Incinerator (MSWI)**

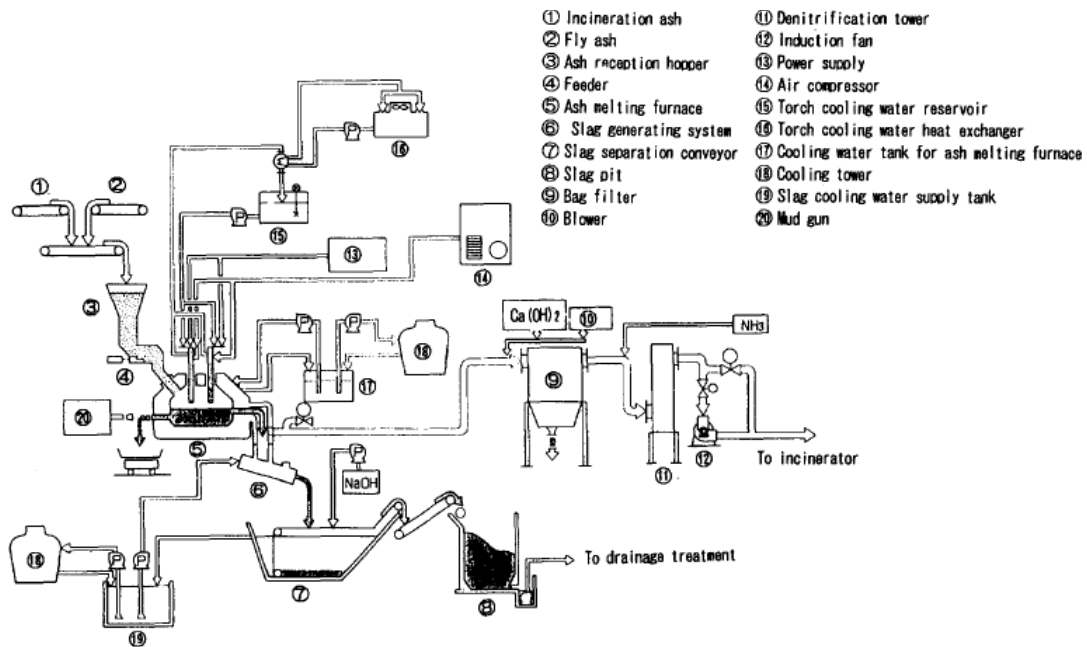
### **1.2.1 Melting**

Melting has been developed since 1990s <sup>37</sup>. It is considered to be a prospective technology for stabilizing MSWI fly ash and bottom ash <sup>37</sup>, because the melting process is to heat the fly ash or bottom ash to fusion temperature, normally above 1200°C, and the residues including fly ash and bottom ash will be transformed to more stable glassy molten slag <sup>37-39</sup>. During the melting process, the organic pollutants decompose and the volume of fly ash and bottom ash can be reduced by 70%. Moreover, the molten slag can be used in the glass- and ceramic industry by some simple pretreatment since the heavy metal has been stabilized in the glassy slag <sup>37-41</sup>. However, now it is not actually put into practice.

There are many types of ash melting furnace developed, such as plasma melting furnace, a reflecting surface-melt furnace, a DC electric joule-heating system, etc <sup>42-45</sup>. Figure 1.2 shows the principal of plasma torch and the plasma ash melting system. There are two methods of using plasma-torch by a counter-electrode, namely the transfer and the non-transfer methods <sup>42</sup>. Electricity is used as the heat source for melting. In the actual plant, the electricity generated by the waste incineration is used.



a) Principal of plasma torch



b) Plasma ash melting system flow chart

Figure 1.2 Schematic illustration of plasma melting system<sup>42</sup>

Melting is effective to reduce the amount of fly ash and the function of stabilization is also very good<sup>39</sup>. However, melting process also produces fly ash and the concentration of heavy metal in that fly ash is larger than in the original fly ash from MSWI<sup>39, 43</sup>. It is more poisonous<sup>39, 43</sup>. Some melting industries send the resulting fly ash to mining industry<sup>39, 46</sup>, to recover the valuable metals by hydrometallurgy method<sup>47</sup>. Some melting industries stabilize it and then send it to the final disposal site such as landfill. Whatever, the fly ash is also a problem. In spite of this, high cost is another

critical problem for melting. According to the “Ledger of municipal solid waste incineration facility (Continuous combustion) (2005)”, among 582 MSWI plants there were only 22 plants adopted melting as the method to treat the fly ash<sup>48</sup>. One of the reasons is the high cost of building a melting plant and the operation. Moreover, the technology needs to be improved in certain areas, e.g., reducing the rate of repairing refractory materials and improving control techniques to ensure stable operation of high-temperature melting<sup>39</sup>.

High concentration of chlorides and other salts with low boiling point will cause troubles for the operation of melting instrument, so normally the fly ash from MSWI should be pretreated<sup>49, 50</sup>.

### 1.2.2 Chemical stabilization

Chemical stabilization is to use chemical reagent such as chelate reagent or other chemical compounds to react with the heavy metal in fly ash to form stable compounds such as chelate complex or precipitation<sup>38, 51-55</sup>. The chemical reagents include ethylenediaminetetraacetate (EDTA), diethylenetriaminepentaacetate (DTPA), organic sulfide, thiourea, phosphate, ferrite, sulfide and so on<sup>51-55</sup>. One of the advantages of chelating agents is that they generally work under moderate pH conditions<sup>55</sup>. EDTA can leach the heavy metals from the ash. NaOH can be used for the leaching of zinc, but the resultant leaching residues should be treated further<sup>53</sup>. Some even added CO<sub>2</sub> to carbonate fly ash to stabilize lead and zinc<sup>56</sup>. As to the phosphate phases likely to precipitate are extremely numerous, particularly Ca phosphates and heavy metal phosphates; Cu, Pb, Zn (CaHPO<sub>4</sub> · 2H<sub>2</sub>O; Ca<sub>4</sub>H(PO<sub>4</sub>)<sub>3</sub> · 2.5H<sub>2</sub>O; Ca<sub>4</sub>(PO<sub>4</sub>)<sub>2</sub>; Ca<sub>5</sub>H(PO<sub>4</sub>)<sub>3</sub>(OH,Cl,F); Cu<sub>4</sub>PO<sub>4</sub>OH; Cu<sub>3</sub>Al<sub>4</sub>(PO<sub>4</sub>)<sub>3</sub>(OH)<sub>9</sub> · 4H<sub>2</sub>O; Cu<sub>6</sub>(NO<sub>3</sub>)<sub>2</sub>(PO<sub>4</sub>)(OH)<sub>7</sub>; (Cu,Zn)<sub>6</sub>(PO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub> · H<sub>2</sub>O, Pb<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>Br; KNa Pb<sub>8</sub>(PO<sub>4</sub>)<sub>6</sub>; β - Pb<sub>9</sub>(PO<sub>4</sub>)<sub>6</sub>; Pb<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>Br; KPb<sub>4</sub>(PO<sub>4</sub>)<sub>3</sub>; PbHPO<sub>4</sub> · H<sub>2</sub>O); (KZn<sub>2</sub>H(PO<sub>4</sub>)<sub>2</sub> · 2H<sub>2</sub>O; α -CaZn<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>; Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> · 4H<sub>2</sub>O; Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>; and (Cu,Zn)<sub>6</sub>(PO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub> · H<sub>2</sub>O)<sup>57</sup>. The mechanism of those diverse compounds to stabilize fly ash is associated with the successive precipitation of increasing stable phosphates<sup>58, 59</sup>, and microenvironment effects. In media rich in calcium, generally present in the form of calcium carbonates, most of the leachable metals are trapped during the precipitation of calcium phosphates containing traces of metals<sup>57</sup>. Some researchers tend to use polymers to stabilize fly ash, especially thermoplastic polymers which encapsulate the residues in a matrix that coats and disperses them have already been used<sup>54</sup>. Unsaturated polyesters (UP) resins are some of the most common thermoset polymers as well as commercial resins<sup>54</sup>.

After chemical stabilization, the heavy metals in fly ash are more stable than their original status in fly ash. However, there is still risk for them to leach out and there is still problem with the chelate complex and deposit. So some chemical treatments are combined with other treatment such as solidification with cement <sup>48</sup>. Moreover, the cost for some chemical reagents is not cheap too, though chemical treatment is much more widely adopted by the continuous MSWIs in Japan <sup>48</sup>.

### 1.2.3 Chemical extraction

The method of chemical extraction is very similar to that of chemical stabilization, which is to use chemical reagent to react with the target element and with the separated deposit or solution to recycle the target elements or stabilize them <sup>38</sup>.

To extract the heavy metal in fly ash is very similar to chemical stabilization <sup>60-64</sup>. The difference is that some will use acid, alkaline or water to extract the heavy metal to get the solution, and then use chemical compounds to form deposits <sup>60-63</sup>. While, after the metals were extracted out as solution, hydrometallurgy method is needed such as electrodialytic method. Here we emphasize more on the purpose of recycling <sup>64, 57</sup>. The target metals are normally Cu, Ni, Co and Zn. There is a typical treatment method for this named “Acid Extraction-Sulfide Stabilization Process (AES process)”, in which water is added to fly ash to convert it slurry, easily soluble heavy metals are extracted by acidic agent, and sodium sulfide is added to slurry to stabilize the remaining heavy metals and thus heavy metal leaching from dewatered cake is prevented <sup>65</sup>.

Though, this method is a little complex and not easy to be carried out into reality, researchers more tend to utilize the sequential extraction of metals in fly ash to study the characteristics of the leaching behavior <sup>67- 71</sup>. The sequential chemical extraction (SCE) was first proposed by Tessier <sup>72</sup>. Now it has been widely used to investigate the physicochemical forms of heavy metals in fly ash. To study the characteristics of fly ashes, the sequential chemical extraction sometimes is combined with other methods such as X-ray diffraction (XRD) analysis and X-ray fluorescence (XRF) analysis <sup>68</sup>. The investigated characteristics of fly ash include the chemical and mineralogical characteristics, releasing characteristics of some special element such as Cr, Cu, Mn, Pb and Zn <sup>70</sup>. And sometimes the steps of SCE will be simplified according to practical purposes <sup>70</sup>.

#### 1.2.4 Cement Solidification

Cement solidification is a method to treat fly ash by using cement as a combining reagent to stabilize the heavy metal through the hydration process of cement in normal temperature<sup>38, 73-80</sup>. It is a cheap disposal method.

Unconfined compressive strength (UCS) is an important factor to evaluate solidification<sup>73</sup>. When ordinary Portland cement (OPC) is blended with fly ash, with the increases of the fly ash to OPC ratio, the water demand of the mixed cement increased and the strength decrease<sup>73</sup>. Lower strength is resulted from the lower Portland cement and much higher waste contents. Generally, a waste/binder ratio of 0.4-0.5 is used with a water/solid ratio of 0.4-0.6. The increase in the binder (cement) content increases the bulk densities because the binders filled the void space of solidified specimen. UCS decreased with increasing crystalline phases<sup>74</sup>. So the initial setting time and hydration process is important in mixing. The standard initial and final setting time reported for OPC should not be less than 45 min and no more than 10 h, respectively<sup>75</sup>. The rate of hydration was reported to be insensitive to temperature over a range of 0-40°C. It is reported that the lower curing temperatures of a lead bearing waste/cement matrix decreases the solubility of lead salts formed in the cement, resulting in an increase in gelatinous coatings on grains<sup>76</sup>. Carbonation is another factor to influence the UCS of the final product. Carbonated stabilization/ solidification (S/S) product develops higher strength in comparison to non-carbonated products<sup>77, 78</sup>. Carbonation involves reaction with phases like AFt/ AFm (hydrated calcium aluminates based on the hydrocalumite-like structure of  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 13-19\text{H}_2\text{O}$ ), calcium silicate hydrates (CSH) gel and calcium hydrate (CH). CSH gels are recognized to play an important role in the fixation of toxic species. The fixation will be significantly altered by carbonation<sup>74</sup>.

The cement-solidified fly ash will mainly be sent at present to landfill and can not be used as the blended cement because of the high concentration of chloride, sulphate and alkali content<sup>80</sup>. As a result, there is still potential environmental risks due to the complex reactions happened in landfill site<sup>81</sup>. And in fact, fly ash solidified with Portland cement presents some disadvantages, namely protection against humidity is required to prevent breaking down and leaching of heavy metals<sup>82-85</sup>. Moreover, the volume of the final product is enlarged because of adding cement and water to form a rigid and porous solid<sup>73-81</sup>, leading to an increase in the cost of disposal<sup>53</sup>. If we want to recycle fly ash as good ingredient or additives in cement, fly ash should be pretreated<sup>86-96</sup>. Also the fly ash washing pretreatment improved the stabilizing

behavior of fly ash-cement mixtures. Because the interaction of fly ash with water leads to a rapid formation of hydrate compounds such as syngenite, gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), ettringite ( $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$ ), calcium hydroxyzincate ( $\text{CaZn}_2(\text{OH})_6 \cdot 2\text{H}_2\text{O}$ ) and laurionite ( $\text{Pb}(\text{OH})\text{Cl}$ )<sup>87, 88</sup>. One draw back of washing process is that adding the washing water to the mixture increases the final water/ solid (w/s) ratio so that decreases the UCS of the final product. Also cement solidification is not suited for Pb-rich fly ashes, since Pb tends to leach out from the solid phase at high pH, which is caused by cement itself<sup>55</sup>.

### 1.2.5 Sintering or Calcinating

Sintering process or calcinating process is similar as melting process but the operation temperature of both processes is lower than the temperature in melting process<sup>38</sup>.

Compared with melting, sintering needs less energy as the heating temperature is lower, while sintering is also effective to stabilize and detoxify fly ash especially to deal with the problem of dioxins<sup>97-99</sup>. Because the operation temperature of both processes is not as high as that in melting process, the volume reduction ratio of final product is less than that of melting process. Another draw back is that the performance of the sintering process is strongly related to the chemical composition of raw fly ash and, in many cases, this process proves to be ineffective for the conversion of raw fly ash into ceramic materials with good mechanical characteristics<sup>86</sup>. Also, pre-treatment had better be adopted<sup>100</sup>.

Some researchers studied sintering as the pretreatment of fly ash to reuse it as a concrete aggregate<sup>101</sup>. However, there also needs a washing pretreatment before sintering, because the sintering of MSW fly ashes proved to be ineffective for manufacturing sintered products for reuse as a construction material, and needs to avoid the adverse chemical characteristics due to sulfate, chloride and vitrified oxide contents contained in fly ashes<sup>101</sup>. On the other hand, the possibility of using sintered products as concrete aggregates is largely depending on the operating conditions adopted for sintering such as the compaction degree of powders, the sintering temperature and time as well as the chemical composition of fly ash. Those factors can affect the type and amount of porosity and, consequently, the specific gravity, mechanical strength and heavy metals leachability of sintered products, as well as their chemical stability in aqueous solutions<sup>101</sup>.

## 1.2.6 Others

Except the single technologies above, some researchers proposed the mixed technology for MSW incineration with multi-purposes.

One of the most famous technology flows is “3R” technology (3R being the German acronym for Rauchgas-Reinigung mit Ruckstandsbehandlung, which means flue gas purification including residue treatment). This process had been developed in the years 1980s by Vehlow<sup>102</sup>. The technology flow is showed in Figure 1.3. The final product, Bottom ash + 3R products will be sent to landfill. The purpose of 3R process is to recover the valuable metals by acid extraction and to stabilize fly ash by returning the residue into the zone of high temperature in the combustion chamber. The 3R technology is suitable for the incinerators equipped with wet scrubber, because the acid which is needed for acid extraction can be obtained from wet scrubber. And binder such as bentonite is necessary to be added to the treated fly ash, which is sent back to the incinerator, to prevent direct release of additional fly ash, which added the cost of 3R process.

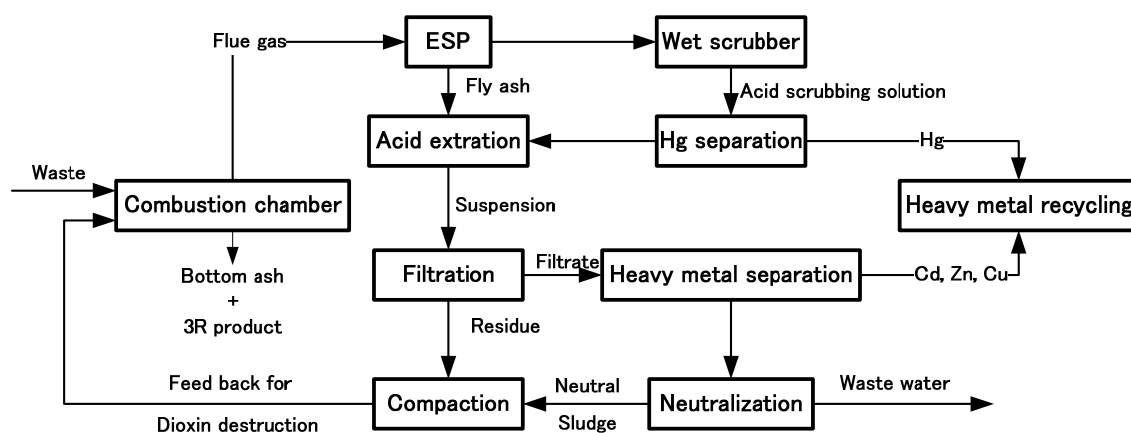


Figure 1.3 Flow schematic of 3R process<sup>102</sup>

While since 1990s to now, some researchers began to study the washing process<sup>86-96</sup>, which is carried out as the pretreatment to reuse fly ash as the raw material or one of the ingredients in cement<sup>93-96</sup>. Some researchers also suggest adding a heat treatment after the washing process, normally sintering or calcinating<sup>86, 101, 103</sup>. Many aspects have been concerned such as the leaching behavior of heavy metals, intensity of the final product, and so on<sup>86-96, 101, 103</sup>.

For the fly ash resulting from neutralization by  $\text{NaHCO}_3$ , the Solvay company has a patent named NEUTREC<sup>®</sup>, which is a recycling system for  $\text{NaHCO}_3$ <sup>104</sup>. Figure 1.4



shows the schematic flow of NEUTREC system. The system needs two sets of particulate capture units: one is special for the original particles in the discharged gas and the other is for the resulting particles by injecting  $\text{NaHCO}_3$  to neutralize the acidic compound in discharged gas. And there still needs to send waste to landfill.

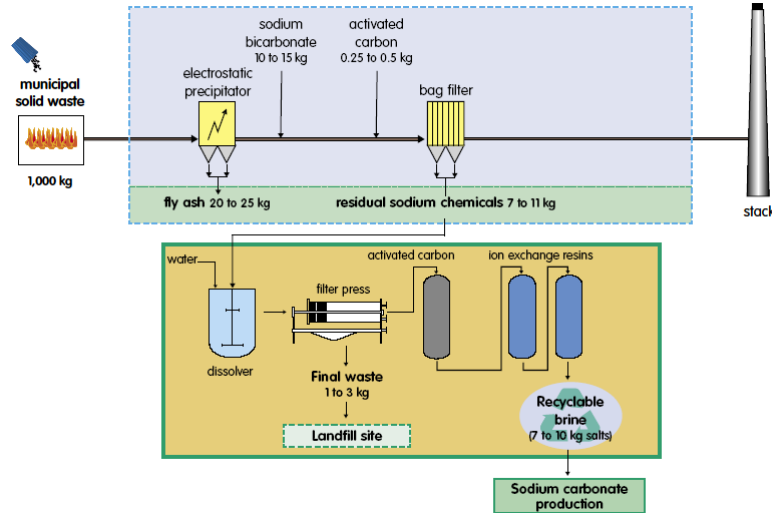


Figure 1.4 Schematic flow of NEUTREC process<sup>104</sup>

## 1.3 Proposal of New Recycling System

### 1.3.1 Sound material-cycle society

Since 2000 Japan has adopted the policy to build Sound Material-Cycle Society, the concept of Reduce, Reuse and Recycle (the “3R” concept) has gradually been the basic principal to follow in every aspects of the solid waste management<sup>105, 106</sup>. I will apply the 3R concept to the management of fly ash from municipal solid waste incineration to make it more positive and less negative influence on environment.

### 1.3.2 Description of the new system

Considering the advantage and disadvantage of the technologies described above and the current situation, I propose a new recycling system of fly ash named “WCCB”; “W” means washing, the first “C” means calcinating, and the “CB” means changing the treated fly ash and bottom ash into raw material in cement industry. In this system I will compare the technological superiority of two kinds of fly ashes resulting from two

alkaline reagents,  $\text{Ca}(\text{OH})_2$  and  $\text{NaHCO}_3$ . The schematic flow is in Figure 1.5:

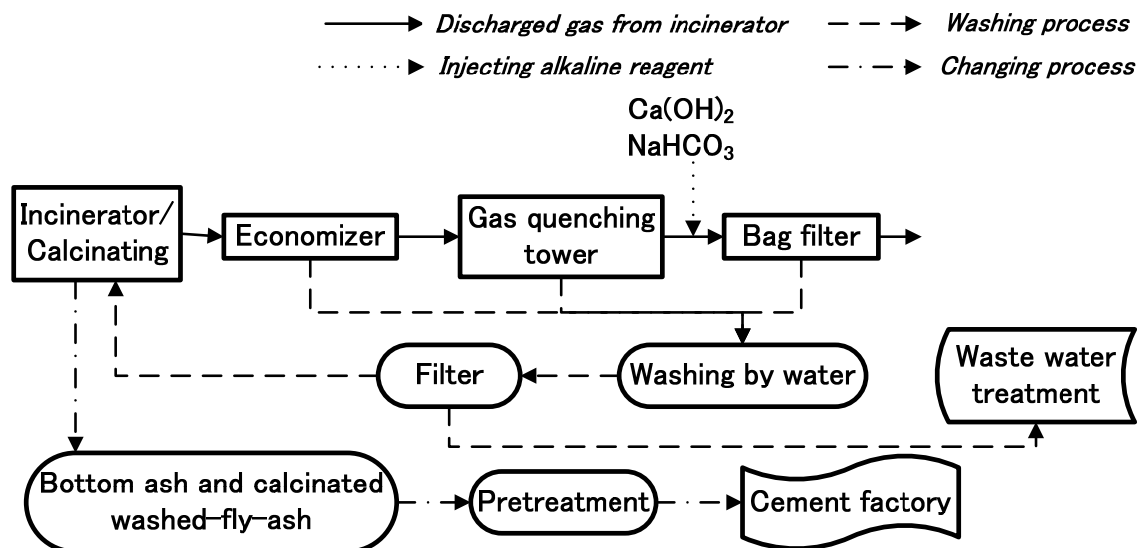


Figure 1.5 Schematic flow of proposed WCCB system

Fly ash from economizer, gas quenching tower and bag filter were firstly washed by water, then being dried, and is sent back to incinerator for calcinating treatment. The treated fly ash together with bottom ash will be used as the raw material in cement industry. In the cement industry, I mean to recycle the heavy metal in the treated fly ash and bottom ash by the original heavy metal recycling system combined with rotary kiln or other equipments. Another important aspect is that in the rotary kiln the temperature is around  $1,200^{\circ}\text{C}\sim 1,500^{\circ}\text{C}$ <sup>107-109</sup>, the residence time is long (The gas retention time is approximately 5s), and the turbulence is strong, which can ensure the complete destruction of even the most stable organic compounds such as PCB and dioxins<sup>107-109</sup>. More over, in Japan, cement industry has utilized many kinds of wastes, such as blast-furnace slag, coal ash, slug, MSW and so on including bottom ash<sup>34, 110, 111</sup>. Some cement industry can also receive fly ash but not so popular because of the high concentration of chlorine in fly ash<sup>112</sup>.

Once WCCB system is well established, this new system will not discharge waste residue such as fly ash and/ or bottom ash out of the system, because they all will be used as the raw material for cement industry. As to the waste water resulting from the washing process, I can pre-treat it by inverse penetration and then discharge it into the municipal sewage system, or I can consider recycling it as the resource for industry salt. I expected to recycle the heavy metal in cement industry with the original recycling system in cement industry.

### 1.3.3 Purposes of this research

As to WCCB system there are two purposes. One is to reduce the amount of discharged second pollution from incineration such as fly ash and bottom ash as much as possible. The other is to reuse the treated fly ash and/ or bottom ash as the raw material in cement industry in maximum ratio.

According to 3R principle, Reduce is the first priority, next is to reuse and the last is to recycle. So to reduce the amount of fly ash is the first purpose of our research. After thinking of reducing the amount of waste produced, I want to reuse the treated residue as much as possible as the raw material in cement industry. Because there is strict limit for chlorine concentration in the cement<sup>113-121</sup>, to decrease the chlorine content becomes the main target for reusing fly ash as the raw material in cement industry.

To achieve the purposes I tried in two directions: one is from the aspect of cleaning production, that is, I tried two kinds of alkaline reagents,  $\text{Ca(OH)}_2$  and  $\text{NaHCO}_3$ ; The other is to find better operation condition for each step of WCCB system.

### 1.3.4 Research content

The WCCB system includes three steps: washing fly ash, calcinating the washed fly ash and changing the treated fly ash and bottom ash into raw material in cement industry. I mean to choose washing as the changing method too. So I will mainly study the first two steps: washing fly ash and calcinating the washed fly ash. Just as I discussed in the purposes of my research, in spite of reducing the amount of final residue, another important target of this research is to lower the chlorine content in the final product. I will compare under the same condition which alkaline reagent is better in amount and chlorine reduction,  $\text{Ca(OH)}_2$  or  $\text{NaHCO}_3$ .

#### 1.3.4.1 Chlorides in fly ash

Many chlorides have been detected in fly ash such as  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{CaCl}_2$ ,  $\text{CaClOH}$ ,  $\text{CaCl}_2 \cdot \text{Ca(OH)}_2$  and so on<sup>62, 57, 79, 89, 90-92, 122-125</sup>. Some researchers reported that insoluble chloride in fly ash is Friedel's salt<sup>126</sup>. Except the chlorides produced in the neutralization process with different alkaline reagents, the incineration itself also forms chlorides and actually some chlorides were detected in raw fly ash from the boiler<sup>125</sup>.

There are many chlorides sources in municipal solid waste <sup>127-131</sup>. Food, especially the cooked food is an important source for chlorides such as NaCl and KCl. Plastics is another considerable source for chlorine <sup>127-131</sup>. In Japan food waste from the manufacturing, distribution and consumption of food, makes up 30% percent of all generated domestic waste <sup>132</sup>. Figure 1.6 shows the variation of component in municipal solid waste from main cities of China <sup>133</sup>. In Sweden kitchen waste occupied 38.9% of the household waste for incineration in 2005 <sup>134</sup>.

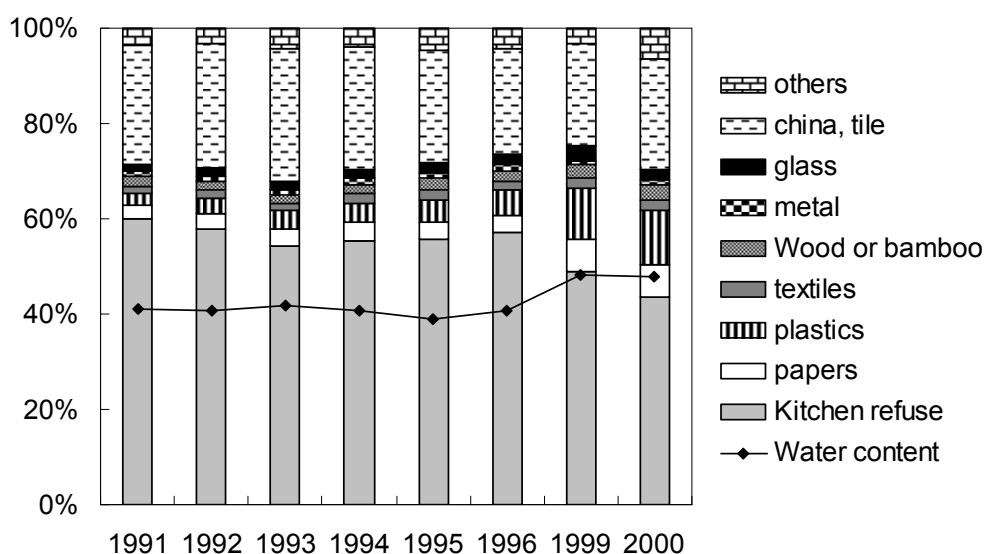


Figure 1.6 The composition of MSW in main cities of China since 1991 to 2000

The concentration of chlorine in fly ash is significant, which is far larger than the limit, 350 ppm, the cement required by industry <sup>135, 136</sup>. I have to reduce the chlorine concentration as much as possible to promote the recycling sue of MSW fly ash.

#### 1.3.4.2 Chlorine and mass reduction methods

Through the research of washing process, it has been found that washing is an effective method to reduce chloride content <sup>86-96</sup>. That means the water-soluble chlorides might contribute most of the chlorides in fly ash. Normally the melting point of chlorides is not so high and is around 1,000°C for such as NaCl, KCl, CaCl<sub>2</sub> and so on <sup>137-138</sup>. However, melting needs larger cost than sintering or calcinating and after all the final product from WCCB system will be sent to the rotary kiln in cement industry, where the temperature is higher than 1,000°C, normally 1,200°C~1,500°C <sup>107-109</sup>. So I would not choose melting as the heating process. I will propose to utilize the zone with high

temperature in the incinerator as the heating part, which might cause calcinating reaction.

Some researchers have developed some technology flow including washing fly ash with calcium phosphate and then calcinating the washed treated fly ash, the aim of which is to extract alkali chlorides in the water phase and retain the metal ions in the solid phase<sup>82</sup>. Figure 1.7 shows the example, the experimental set-up used in previous study by other researchers. However, I would like to use only water in washing process. One reason is to decrease the cost and the other reason is I have different purposes.

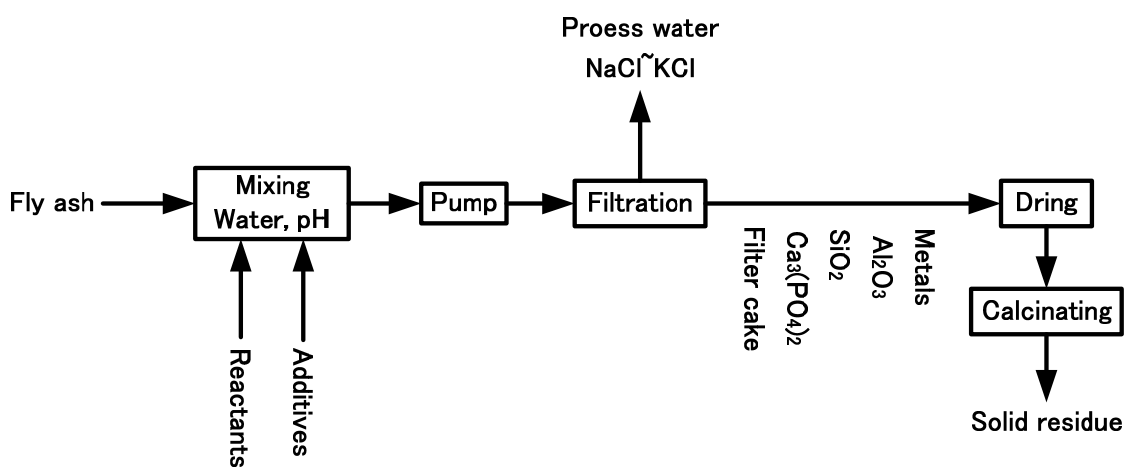


Figure 1.7 Experiment set up<sup>82</sup>

In addition to the optimization of the parameters in washing and calcinating process, it should be decided what alkaline reagents is to be used in the air pollution control (APC) system of incinerator. Different alkaline reagents will result in fly ash of different characteristics as well as the corresponding mass amount<sup>139-142</sup>. Normally the sodium-based alkaline reagent is more efficient than calcium-based alkaline reagent to neutralize the acid compound in the discharged gas<sup>139, 140</sup>. The higher effectiveness of sodium-based sorbents (Na-sorbents) is particularly remarkable for hydrogen chloride, whose concentration must always be kept below the values set by the environmental regulations<sup>140</sup>. Moreover, there is abundant CO<sub>2</sub> in the discharged gas, which affects the behavior of HCl sorption by Ca-sorbents but does not influence the performance of Na-sorbents in the temperature range 300-600°C<sup>141</sup>. As a result, I decided to compare the results of Ca-sorbents with Na-sorbents in the WCCB system to find out which is better in WCCB system. Currently, the most popular Ca-sorbents is Ca(OH)<sub>2</sub>, while the Na-sorbent put into practice is NaHCO<sub>3</sub>, though the number of incinerators which use NaHCO<sub>3</sub> is much less than that of incinerators which use Ca(OH)<sub>2</sub>. As a result, I would

compare those two alkaline reagents:  $\text{Ca}(\text{OH})_2$  and  $\text{NaHCO}_3$ .

## 1.4 Structure of the doctor dissertation

The contents of this doctor dissertation include the research of washing and calcinating process in the WCCB system. I will explain the research results along with the order of the technology flow of the WCCB system. First I discuss the washing process and then the calcinating process. The total research results are described in five chapters. Except this chapter, there are other four chapters.

The first chapter, this chapter, gathered the background information of this research: Such as why we should protect our environment, the importance of municipal solid waste management, current problems of incineration as one of the main technologies to treat MSW, especially the problem on fly ash. Then I listed the various intermediate treatment methods of fly ash and compared the superiorities and draw backs. To build the Sound Material-Cycle Society, I proposed a new technological recycling system for fly ash, named WCCB, and set the research purposes.

The second chapter is to discuss the experiment condition of the washing process. Firstly, I use raw fly ash from the boiler of the incinerator to do the preliminary experiments to find the critical factors of washing experiment. Based on the results of preliminary experiments, I design the washing experiment conditions. I apply the same washing experiment condition to three kinds of fly ashes: raw fly ash from the boiler of incinerator, fly ash collected in a bag filter with the injection of calcium hydroxide for acid gas removal (CaFA) and fly ash collected in a bag filter with the injection of sodium bicarbonate for acid gas removal (NaFA). With the results of those parallel experiments, it is possible for me to find the washing characteristics of those three kinds of fly ash and then I can find the difference between the injection of  $\text{Ca}(\text{OH})_2$  and the injection of  $\text{NaHCO}_3$  in the washing process. I will set the most acceptable washing condition for the next step——calcinating.

The third chapter is to try to study the mechanism of removing chlorides from the three kinds of fly ashes in washing experiments. Firstly I use the method of combining X-ray absorption near edge structure (XANES)<sup>143-145</sup> with X-ray diffraction (XRD)<sup>146-148</sup> to determine the chloride speciation in the three kinds of fly ashes. Then I will apply the same method to the residues from the washing experiments in Chapter 2, to explain the chloride behavior in those three kinds of fly ashes in the washing experiments. With those results, I will explain the phenomena observed in the washing experiments, and

examine which alkaline reagent is better,  $\text{Ca}(\text{OH})_2$  or  $\text{NaHCO}_3$ , for recycling use of fly ash based on the governing mechanism.

The fourth chapter is about the calcinating process in the WCCB system. Similar as the procedures used in washing experiments, first step is the preliminary experiments to find the critical parameters for calcinating, and then I will process the main experiments for all the three kinds of washed fly ashes. Comparing the final results, I will determine the most acceptable condition for the calcinating process. I also discuss on the mass balance of chlorine in the calcinating process.

The fifth chapter is the conclusions. I will summarize the results obtained in this research and recommend further research.

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## 2 RESEARCH OF WASHING PROCESS

### 2.1 Introduction

Washing is the first step in the WCCB system. There are two main reasons for washing: to cut down the amount of residue fed back to the incinerator, and to wash out as much chloride as possible. Other than optimizing the washing conditions, another way to achieve weight reduction of fly ash is to replace calcium hydroxide with some other alkaline material used in the dry scrubber. While  $\text{Ca}(\text{OH})_2$  is widely used for acid gas treatment, sodium bicarbonate has been recently introduced in some incineration plants<sup>1-3</sup>. Under the same general conditions, the amount of  $\text{Ca}(\text{OH})_2$  required to remove a specific amount of HCl is much larger than the amount of  $\text{NaHCO}_3$  required to remove HCl from the flue gas. I expect that replacing  $\text{Ca}(\text{OH})_2$  by  $\text{NaHCO}_3$  will lead to a weight reduction of fly ash. I will investigate the characteristics of three types of fly ash in washing experiments to obtain more information to confirm the superiority of  $\text{NaHCO}_3$ . The three types of fly ashes are fly ash collected in a bag filter with the injection of  $\text{Ca}(\text{OH})_2$  for acid gas removal (CaFA), the fly ash collected in a bag filter with the injection of  $\text{NaHCO}_3$  for acid gas removal (NaFA), and raw fly ash collected from the boiler incinerator (RFA). Because RFA is the fly ash which was not affected by the injection of alkaline reagents, it is necessary to conduct more obvious comparison between CaFA and NaFA. The washing characteristics of NaFA have never been reported before. The reason why we must reduce the amount of chloride is related to the fact that the fly ash is to be used as the raw material in cement industry. It is well known that chloride in cement will corrode steel<sup>4,5</sup>. It is also known that chloride cations affect the corrosion rate of steel in concrete;  $\text{CaCl}_2$  is more corrosive than NaCl or KCl<sup>6</sup>, for example. This points to another potential advantage of using  $\text{NaHCO}_3$ .

I will determine the optimum conditions for washing fly ash produced with either  $\text{Ca}(\text{OH})_2$  or  $\text{NaHCO}_3$ . There have been a number of studies on washing fly ash or bottom ash<sup>7-13</sup>. In those previous researches, the liquid to solid (L/S) ratio ranged from 2 to 100 while the mixing time ranged from 10 min to 1 hr. In order to make our research more reasonable, before the main experiments, I processed preliminary

experiments of RFA to find out the hierarchical structure of parameters for washing experiments. Then I design the main experiments.

## 2.2 Experiment material and method

### 2.2.1 Experiment material

Three types of fly ashes used: CaFA, NaFA and RFA. The composition of the three types of fly ash was examined by X-ray fluorescence (XRF-1700, Shimadzu Corporation), and inductively coupled plasma-atomic emission spectrometry (ICP-AES, IRIS Intrepid, Optronic Co., Ltd.). The results are shown in Table 2.1.

Table 2.1 Element content of CaFA, NaFA and RFA (weight %)

Element	CaFA	NaFA	RFA	Element	CaFA	NaFA	RFA	Element	CaFA	NaFA	RFA
<b>O</b>	24.6	13.2	37.3	<b>K</b>	3.38	5.84	2.99	<b>Fe</b>	1.24	0.713	2.32
<b>Si</b>	2.68	1.28	4.97	<b>Na</b>	3.46	18.5	2.97	<b>Zn</b>	0.390	0.893	0.223
<b>C</b>	7.55	8.17	3.24	<b>Ti</b>	0.821	0.535	1.51	<b>Cu</b>	0.0639	0.147	0.238
<b>Cl</b>	19.6	37.3	6.36	<b>Mg</b>	0.722	0.341	1.12	<b>Pb</b>	0.212	1.23	0.387
<b>S</b>	1.81	1.31	3.31	<b>P</b>	0.241	0.179	0.666	<b>Br</b>	0.269	0.914	0.111
<b>Ca</b>	28.2	10.2	24.7	<b>Al</b>	4.30	5.92	3.99				

### 2.2.2 Experiment method

Ion exchanged water (IEW) was used as the washing solution. The fly ash was mixed with IEW by a vortex mixer (Iuchi Seiedo, Co, Ltd.) under different liquid (ml) to solid (g) (L/S) ratio and separated by centrifuge (Himac CT4, Hitachi) for 15 min at 3,000 rpm after washing. The washed residue was dried in an oven at 105°C for 24 hours.

To decide the main experiment conditions, I first processed preliminary experiments to discuss the influence of parameters of mixing time, L/S ratio and washing frequency on the final results. Based on the results of preliminary experiments, I design the main experiment conditions.

#### 2.2.2.1 Preliminary experiments

In the preliminary experiments, only RFA was used. The parameters of interest are L/S

ratio, mixing time and washing frequency.

#### I. Discussion of the mixing time

In preliminary experiment I I varied the mixing time as 10 minutes, 30 minutes and 1 hour. The mixing speed was fixed at 150 rpm. I also compared the difference of the results between L/S of 5 and L/S of 10. The amount of fly ash used for every experiment is fixed at 10 gram. Therefore for example L/S of 5 means that 50ml IEW was used to wash. The detailed experiment condition is shown in Table 2.2

Table 2.2 Experiment conditions for preliminary experiment I

Code	L/S	Mixing time	Mixing speed	Code	L/S	Mixing time	Mixing speed
P-1#	5	10 minutes	150 rpm	P-4#	10	10 minutes	150 rpm
P-2#	5	30 minutes	150 rpm	P-5#	10	30 minutes	150 rpm
P-3#	5	1 hour	150 rpm	P-6#	10	1 hour	150 rpm

I checked the weight percent of the residue after each experiment and marked it as “R”. The definition is Formula 2.1. The chlorine content in the residue was determined by XRF, and the results are in Figure 2.1.

$$R = \frac{Mass_{washed-dried}}{Mass_{origin}} \times 100\% \quad (2.1)$$

Where  $Mass_{origin}$  is the dry weight of fly ash used in each experiment and  $Mass_{washed-dried}$  is the amount of dry residue after the fly ash was washed.

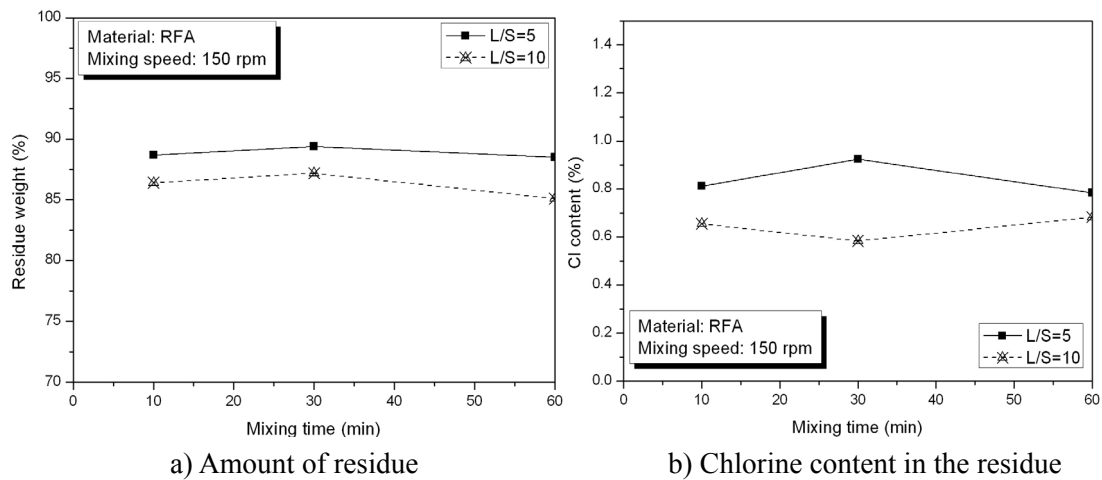


Figure 2.1 Experiment results of preliminary experiment I

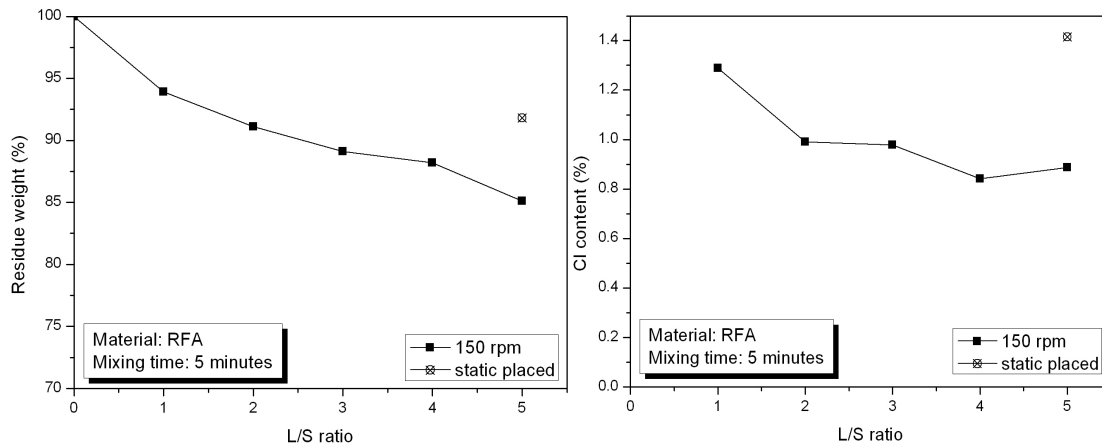
Figure 2.1 shows that there is not so much difference among the results of P-1#, P-2# and P-3#, or P-4#, P-5# and P-6#, and the trend is not so clear. While, the difference caused by the L/S seems more obvious and manifest.

## II. Discussion of L/S ratio

Based on the results from preliminary experiment I, I fixed the mixing time as 5 minutes and varied the L/S ratio from 1 to 5 for the preliminary experiment II. Same as preliminary experiment I, 10 gram RFA was used in every experiment. I also did one experiment to check the function of mixing speed in single-washing. Table 2.3 shows the condition of preliminary experiment II. Figure 2.2 presents the corresponding results.

Table 2.3 Experiment conditions for preliminary experiment II

Code	L/S	Mixing time	Mixing speed	Code	L/S	Mixing time	Mixing speed
P-7#	1	5 minutes	150 rpm	P-10#	4	5 minutes	150 rpm
P-8#	2	5 minutes	150 rpm	P-11#	5	5 minutes	150 rpm
P-9#	3	5 minutes	150 rpm	P-12#	5	5 minutes	Static placed



a) Weight of residue

b) Chlorine content in the residue

Figure 2.2 Experiment results of preliminary experiment II

Figure 2.2 shows that with the increase of L/S ratio the residue weight decreases and the chlorine content becomes lower. Comparing to the result without mixing, the results with mixing have less residue weight and less chlorine left.

### III. Discussion of washing frequency

I also processed double-washing experiments. The experiment condition and corresponding results are shown in Table 2.4. Obviously double washing gives smaller residual and chlorine content.

Table 2.4 Experiment condition and result for preliminary experiment III

Code	L/S	Mixing time	Mixing speed	Washing frequency	Residue percentage/ %	Cl content/ %
P-13#	10	30 minutes	150 rpm	2	81.9	0.477
P-5#	10	30 minutes	150 rpm	1	87.2	0.584

#### 2.2.2.2 Final experiment condition

Based on the results from preliminary experiments I designed the main experiment condition. I will process single-washing, double-washing and triple-washing experiments. Table 2.6, 2.7 and 2.8 show the detailed experiment conditions.

Table 2.6 Experimental design of the single-washing experiments

Code	L/S	Experimental conditions	Code	L/S	Experimental conditions
1#	0	Fly ash	5#	5	150 rpm, 5 min
2#	2	By glass rod, 5 min	6#	6	150 rpm, 5 min
3#	3	150 rpm, 5 min	7#	8	150 rpm, 5 min
4#	4	150 rpm, 5 min	8#	10	150 rpm, 5 min

Table 2.7 Experimental design for the double-washing experiments

Code	L/S	Experimental conditions	Code	L/S	Experimental conditions
9#	3-3		17#	3-3	
10#	3-5	150 rpm, 5 min -	18#	3-5	150 rpm, 5 min -
11#	3-7	150 rpm, 30min	19#	3-7	150 rpm, 10 min
12#	3-10		20#	3-10	
13#	3-3		21#	3-3	
14#	3-5	150 rpm, 5 min -	22#	3-5	150 rpm, 5 min -
15#	3-7	250 rpm, 10 min	23#	3-7	250 rpm, 30 min
16#	3-10		24#	3-10	

Table 2.8 Experimental design for the triple-washing experiment

Code	L/S	Experimental conditions
25#	3-3-3	150 rpm, 5 min – 150 rpm, 10 min – 150 rpm, 10 min

The purpose of the single-washing experiments is to find a suitable L/S ratio for the first step of the double-washing experiments, and to compare the different washing characteristics of CaFA and NaFA. The purpose of the double-washing experiments is to determine the suitable conditions for the first and second step of the triple-washing experiments, and to provide a comparison for the single-washing results. The triple-washing experiments were performed to determine if triple washing resulted in a significant improvement over double washing.

I used 20 g of fly ash in each experiment. An L/S ratio of 5 indicates that 100 ml water was used to wash 20 g of fly ash. In the double-washing and triple-washing experiments, the L/S ratio value was based on the 20 g of fly ash used in the first step. For example, the L/S ratio of 3-3-3 shown in Table 2.8 means 20 g of fly ash was washed by 60 ml of ion exchanged water in each step of the triple-washing experiment. Note that for an L/S ratio of 2 (refer to Table 2.6), the amount of water is too small to use the mixer, so those samples were stirred manually with a glass rod.

## 2.3 Experiment results and discussions

The washing process is the first step of the WCCB system, aiming at reducing the weight of residue and the chlorine content. In this section, I discuss how well this worked.

## 2.3.1 Single-washing experiments

### 2.3.1.1 Reduction of weight and chloride content

In this section, I refer to the washed fly ash as residue. Figure 2.3 shows the change in the residue weight percent mass and chlorine content in the residue as a result of the single-washing experiments.

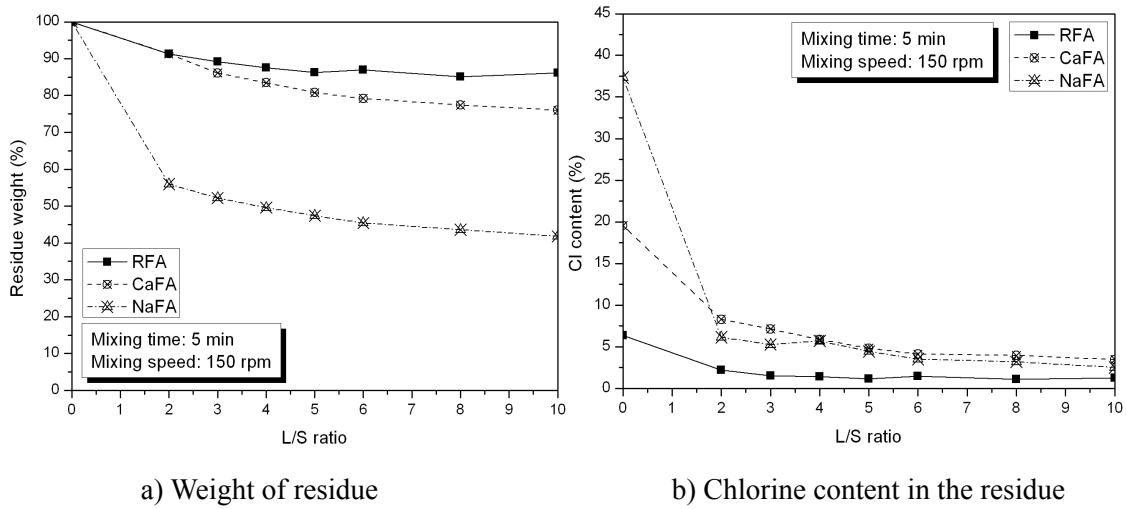


Figure 2.3 Results of single-washing experiments

The residue mass percent was also calculated with Formula 2.1. The amount of chlorine washed out was calculated from Formula 2.2

$$\frac{Mass_{origin} \times C_{Cl,origin} - Mass_{washed-dried} \times C_{Cl,washed-dried}}{Mass_{origin} \times C_{Cl,origin}} \times 100\% \quad (2.2)$$

Where  $C_{Cl,origin}$  is the chlorine concentration in the fly ash before the washing experiments and  $C_{Cl,washed-dried}$  is the chlorine concentration in the residue after the fly ash was washed and then dried.

Obviously the larger water (the larger L/S ratio) resulted in the less residue and less remaining chloride. For an L/S ratio of 10, the percent residue weight of CaFA, NaFA and RFA are 86.1%, 76.0% and 41.8%, respectively. Thus, single washing reduced the amount of RFA by about 14.0%, CaFA by about 24.0% and NaFA by 58.2%. In other words, there was almost twice as much CaFA residue than NaFA under the same



conditions. Thus, 83.3% of the chlorine in RFA, 86.6% of the chlorine in CaFA and 97.2% of the chlorine in NaFA can be washed out into water. The amount of chlorine remaining in the residue of CaFA-8# was 2.5 times larger than that in the residue of NaFA-8#. For L/S ratios above 4, the decrease was not as rapid as for L/S ratios in the range of 1–3; this was more significant for CaFA and RFA. The decreasing slope as the left derivative of the curves was calculated using Formula 2.3 and is shown in Table 2.9.

$$f'_-(x_1) = \frac{y_{x_2} - y_{x_1}}{x_2 - x_1} \quad (x_2 < x_1 : x_1 = 2, 3, 4, 5, 6, 8, 10; x_2 = 0, 2, 3, 4, 5, 6, 8) \quad (2.3)$$

Where  $x_1, x_2$  is the L/S ratio in consecutive single washing experiments and  $y_{x_1}, y_{x_2}$  is the corresponding percent residue mass or chlorine content of each washing experiments.

Table 2.9 Decreasing rate of residue weight percentage curve and Cl% curve for CaFA

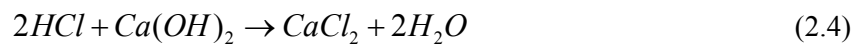
L/S	2	3	4	5	6	8	10
<b>Residue</b>	-7.0	-5.3	-2.6	-2.7	-1.6	-1.8	-1.4
<b>Cl%</b>	-5.6	-1.2	-1.2	-1.1	-0.73	-0.08	-0.25

Table 2.9 indicates that an L/S ratio of 3 in the residue curve was a turning point. Therefore, the L/S ratio of 3 is used for the first stage of the double-washing experiments.

### 2.3.1.2 Comparison of NaFA and CaFA

I assumed that the HCl and particulate concentrations in the flue gas were 700 mg/m<sup>3</sup>N and 3 g/m<sup>3</sup>N, respectively, and that the alkali reagent condition was such that the molar ratio of HCl:Ca(OH)<sub>2</sub> and HCl:NaHCO<sub>3</sub> were 1:2.8 and 1:1.2, respectively<sup>1, 2</sup>. Therefore, in 1 m<sup>3</sup>N discharge gas, there was 700 mg of HCl and 3 g of particulate that was RFA.

Writing the reaction for HCl and Ca(OH)<sub>2</sub>,



I can calculate the reacted HCl molar amount as

$$m_{HCl} = \frac{700mg}{36.5g/mol} = 0.0192mol \quad (2.5)$$

The reacted Ca(OH)<sub>2</sub> molar amount is

$$m_{Ca(OH)_2} = 2.8 \times m_{HCl} = 2.8 \times 0.0192 \text{ mol} = 0.0538 \text{ mol} \quad (2.6)$$

The produced  $CaCl_2$  molar amount is

$$m_{CaCl_2} = \frac{m_{HCl}}{2} = 0.0192 \text{ mol} \div 2 = 0.0096 \text{ mol} \quad (2.7)$$

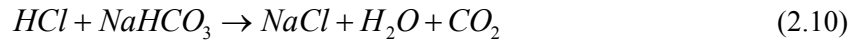
The corresponding mass of  $CaCl_2$  is

$$M_{CaCl_2} = m_{CaCl_2} \times 111 \text{ g/mol} = 0.0096 \text{ mol} \times 111 \text{ g/mol} = 1.07 \text{ g} \quad (2.8)$$

The remaining mass of  $Ca(OH)_2$  is

$$\begin{aligned} M_{Ca(OH)_2, \text{left}} &= (m_{Ca(OH)_2} - \frac{m_{HCl}}{2}) \times 74 \text{ g/mol} \\ &= (0.0538 \text{ mol} - 0.0096 \text{ mol}) \times 74 \text{ g/mol} = 3.27 \text{ g} \end{aligned} \quad (2.9)$$

Therefore, including the 3 g of RFA, there will be 7.34 g of CaFA. Writing the reaction for HCl and  $NaHCO_3$ ,



By the same deduction process of CaFA, 4.44 g of NaFA will form for 1  $m^3$ N discharged gas. Because the percent residue weight of CaFA and NaFA in the washing experiments for an L/S ratio of 10 was 76.0% and 41.8%, respectively, the residual CaFA and NaFA after washing were 5.58 g and 1.86 g. If we use  $NaHCO_3$  instead of  $Ca(OH)_2$  as the alkaline reagent and wash the fly ash, we can reduce the amount of fly ash returned to incinerator by 33.3%.

Using the above data, the Cl content in the residual CaFA and NaFA after washing was 0.192 g and 0.0470 g, respectively. Therefore we can reduce the amount of Cl returned to the incinerator by 75.5% if we use  $NaHCO_3$  and wash the fly ash. Overall,  $NaHCO_3$  is much better in reducing the ash volume and the amount of Cl, both of which are advantageous for the WCCB system.

## 2.3.2 Double and triple-washing experiments

### 2.3.2.1 Experiment results

The main purpose of the double-washing experiment is to find suitable washing conditions for CaFA, NaFA and RFA. Figure 2.4 shows the percent residue weight and Cl content of CaFA, NaFA and RFA in the double- and triple-washing experiments. Appendix No.1 gives the exact result of each experiment. In the double-washing experiments, the weight of RFA was reduced by at most 18.2%, the weight of CaFA

was reduced by 26.7%, and the weight of NaFA was reduced by 65.4%. In the double-washing experiments, the lowest concentrations of Cl for CaFA, NaFA and RFA were 0.647%, 1.08% and 1.35%, respectively.

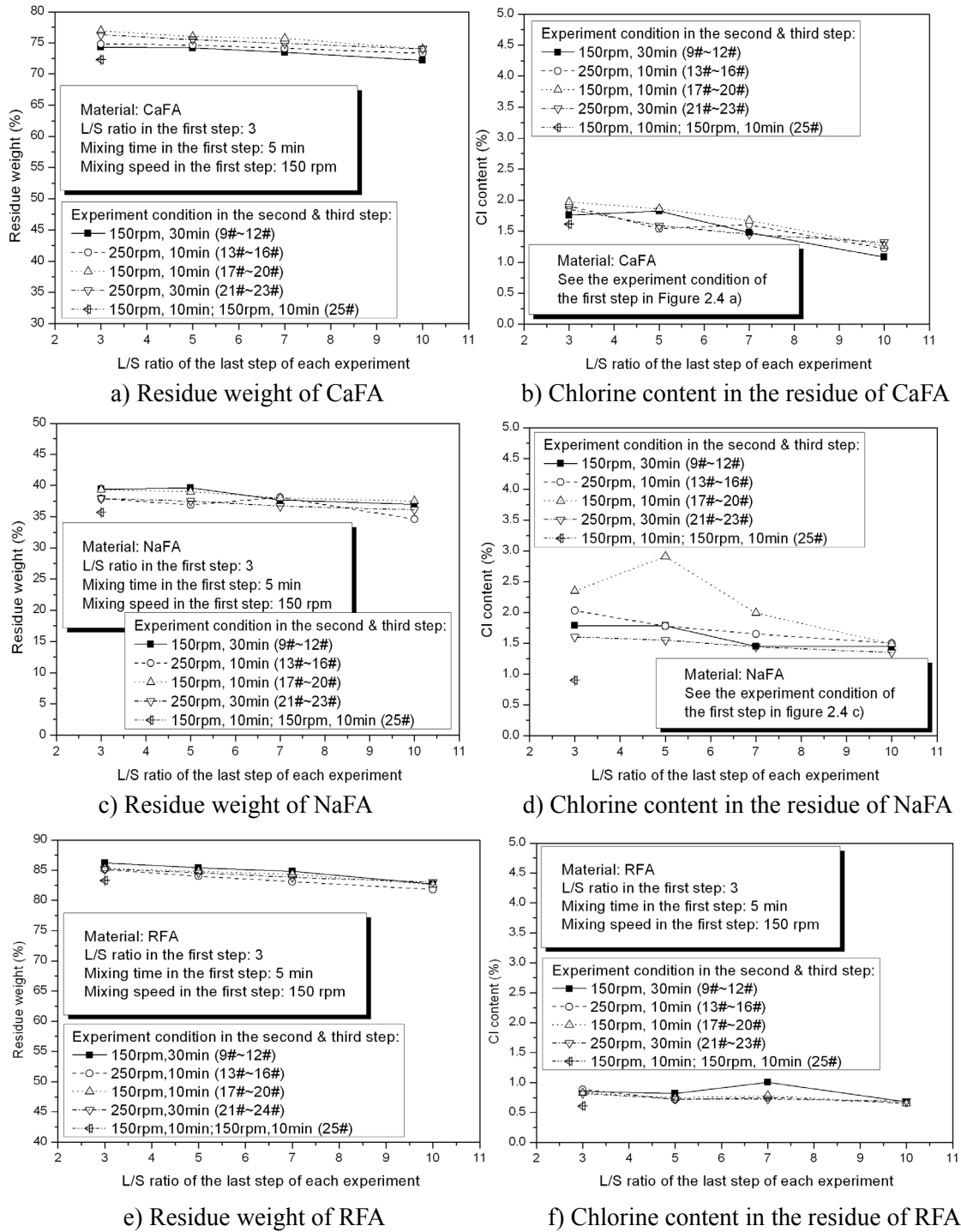


Figure 2.4 Double and triple washing experimental results

### 2.3.2.2 Comparison of double-washing and single-washing experiments

As in the single washing experiments, a larger amount of washing water reduced more residue weight and the Cl content in the double-washing experiments. However, the decrease in either the residue weight or the Cl content was not as pronounced as in the single-washing experiments. For example, in the CaFA double-washing experiments, the difference in the percent residue weight between the CaFA-17# and CaFA-20# experiments was 2.90%, which is the maximum value for CaFA-9# and CaFA-12#, CaFA-13# and CaFA-16#, CaFA-17# and CaFA-20#, and CaFA-21# and CaFA-24#. The L/S ratio of CaFA-17# in the second step was 3, while that of CaFA-20# was 10. In the CaFA single-washing experiments, the difference in the percent residue weight between CaFA-3# (L/S ratio=3) and CaFA-8# (L/S ratio=10) was 10.1%, which is 2 times larger than the 2.90% result. The same result was obtained for variations in the chloride content. The difference between the chloride content in the residue of CaFA-17# and the residue of CaFA-20# is 0.71%, which is 1/5th of the difference between the chloride content in the residue of CaFA-3# and the residue of CaFA-8#, 3.67%. Similar results were also obtained for NaFA. It is clear that most of the easily soluble compound had been dissolved into water in the first washing, and the remaining compound was difficult to dissolve in the second washing. As a result, the L/S ratio did not have a large impact on the second washing. The same was true for the mixing time and speed.

In all double-washing experiments for each L/S ratio in the second step, the maximum difference of residue weight in the RFA residue and the NaFA residue mass were 4.4% and 2.4% respectively, while that of the RFA chlorine content and the NaFA chlorine content were 0.242% and 1.42% respectively.

### 2.3.2.3 Washing frequency

A comparison of the single-washing and double-washing experiments shows that the washing frequency is more important than other factors such as the L/S ratio, mixing time, or mixing speed. To emphasize this finding, I examine the results of the triple-washing experiments.

Figures 2.4 (c) and 2.4 (d) clearly show that the percent residue weight and the chlorine content in the NaFA residue are much less after triple-washing than after double-washing. For CaFA and RFA, the extra washing is not as effective. I compared the percent residue weight and the amount of chlorine washed out from the CaFA-9#,

CaFA-19#, and CaFA-25# experiments and summarized the results in Table 2.10. The CaFA-25# experiment has the least weight residue and the most chlorine. Comparing the experimental conditions of CaFA-9# and CaFA-25#, the total mixing time of CaFA-9# is 35 minutes and that of CaFA-25# is 25 minutes. Thus washing frequency is more effective than the mixing time. Similarly, comparing the experimental conditions of CaFA-19# and CaFA-25#, it can be found that the total water used in the CaFA-19# experiment is 100 ml compared to 90 ml in the CaFA-25# experiment. Since a larger volume of water gave worse results, the washing frequency is more important than the L/S ratio. If the data of RFA-9#, RFA-19# and RFA-25# were analyzed, I can get the same conclusion and I show the corresponding data in Table 2.10 too. Since the washing frequency is more critical than the L/S ratio, mixing time, or mixing speed, double-washing is necessary.

Table 2.10. Comparison of results for CaFA-9#, 19#, and 25# and RFA-9#, 19# and 25#

Code	Experimental conditions	Residue weight (%)	Chlorine washed out (%)
CaFA-9#	3:1, 150 rpm, 5 min – 3:1, 150 rpm, 30 min	74.3	93.3
CaFA-25#	3:1, 150 rpm, 5 min – 3:1, 150 rpm, 10 min – 3:1, 150 rpm, 10 min	72.3	94.1
CaFA-19#	3:1, 150 rpm, 5 min - 7:1, 150 rpm, 10 min	75.7	80.1
RFA-9#	3:1, 150 rpm, 5 min – 3:1, 150 rpm, 30 min	86.2	88.4
RFA-25#	3:1, 150 rpm, 5 min – 3:1, 150 rpm, 10 min – 3:1, 150 rpm, 10 min	83.3	92.0
RFA-19#	3:1, 150 rpm, 5 min - 7:1, 150 rpm, 10 min	84.3	89.7

#### 2.3.2.4 Optimization of experimental conditions

Based on the results of the single-, double-, and triple-washing experiments, it is possible to determine the most acceptable condition for each type of fly ash to proceed to the next step of the WCCB system: the calcination process.

##### *I. Discussion of CaFA*

As shown in Figure 2.4(a) and 2.4(b), the minimum percent residue weight obtained after double-washing, which occurred in the CaFA-12# experiment, is almost the same as the percent residue weight obtained after the triple-washing experiment. The minimum chlorine content after double-washing also occurred in the CaFA-12# experiment, but this value is 0.53% less than that of the triple-washing experiment. The

mixing time of the CaFA-12# experiment is 10 min longer and the L/S ratio is 1 larger than the conditions used for the triple-washing experiment. However, the extra time and the water consumed to separate the residue from the mixture after the second washing of the triple-washing experiment, followed by drying the residue, contribute only to a marginal improvement.

However, although the percent residue weight and chlorine content of CaFA-12# are the minimum values among double-washing experiments, just as I have analyzed in the former section that the difference among the results of double-washing experiments is not so significant. Considering the amount of waste water and time consumption, and that there are other two steps of treatment followed after washing, I suggest the washing condition of CaFA-17# as the most acceptable washing condition for WCCB system of CaFA.

## *II. Discussion of NaFA*

NaFA behaves somewhat different from CaFA. The minimum percent residue weight after double-washing occurred in the NaFA-16# experiment (refer to Figure 2.4). This value is 1.1% less than the result of the triple-washing (NaFA-25#) experiment, which has the second lowest value. The minimum chlorine content after double-washing occurred in the NaFA-25# (triple-washing) experiment, which is 0.45% less than that of the NaFA-24# (double-washing) experiment and 0.60% less than that of the NaFA-16# (double-washing) experiment.

While, NaFA-16# conditions include a mixing speed of 250 rpm, which consumes much more energy. As to NaFA-25# (triple-washing) experiment, same reason as that explained in the discussion of CaFA that the amount of waste water, time consumption of triple-washing and other double-washing experiments, and followed treatment, I would like to adopt NaFA-17# as the washing condition for WCCB system of NaFA. With this condition, I can compare the results directly with CaFA.

## *III. Discussion of RFA*

RFA acts a little like NaFA. RFA-16# experiment has the minimum percent residue weight, 81.8%, while RFA-25# experiment (triple-washing) is of the minimum chlorine content, 0.610%. The minimum percent residue weight is 0.8% less than the second lowest value (RFA-20#), while the minimum chlorine content is 0.037% less than the second lowest value (RFA-20#). Similar reason as that explained in the discussion of NaFA, I will select the experimental condition of RFA-17# as the washing condition for WCCB of RFA.

## 2.4 Conclusion

In washing experiments for the WCCB system, I found that the CaFA and NaFA have different characteristics. Under the same washing conditions, the percent residue weight of NaFA is always less than that of CaFA because there are more soluble compounds in NaFA than in CaFA. Although the chlorine content in the washed residue of NaFA is comparable to that in the washed residue of CaFA, the percent residue weight of NaFA is much less than that of CaFA, so the soluble chloride portion in NaFA is also more than that in CaFA.

It is clear that washing frequency has a greater influence on reducing the amount of residue and the chlorine content than the L/S ratio, mixing time, or mixing speed.

According to the results of the double- and triple-washing experiments for RFA, CaFA and NaFA, the 17# experimental conditions (3:1, 150 rpm, 5 min; 3:1, 150 rpm, 10 min) are suggested to be the final washing condition for washing process. After the three kinds of fly ashes are treated by this condition, the resulting residues will be under calcinating process.

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## **3 CHLORIDE REDUCTION MECHANISM IN WASHING PROCESS OF FLY ASHES**

### **3.1 Introduction**

The final product from WCCB system is to be the raw material in the cement industry. While to be the raw material in cement industry, the chlorine content is a very important factor to be concerned. One aspect is that the migration of chloride into concrete accelerates the corrosion of embedded steel <sup>1</sup>, and different chloride cations corrode steel in concrete to different degrees;  $\text{CaCl}_2$  has a more deleterious effect than either  $\text{NaCl}$  or  $\text{KCl}$  <sup>2</sup>. Another issue is that cement kilns operate under alkaline conditions because of abundant existence of  $\text{CaO}$  and  $\text{CaCO}_3$ . Thus, virtually all chlorine entering a kiln is in the form of  $\text{CaCl}_2$ ,  $\text{NaCl}$ , or  $\text{KCl}$  and will sublime in the calcination zone and recrystallize in the decarbonization zone, which may lead to blockages, e.g., in cyclone pipes, resulting in kiln shutdown <sup>3,4</sup>. To maximize the reuse of fly ash, the chloride content in fly ash must therefore be reduced as much as possible.

In the previous researches and our research I have found that washing is an effective method to reduce chlorine content in fly ash <sup>5-8</sup>. However, there are few researches which find out the reason or explained the corresponding mechanism <sup>5-8</sup>, though some studies have assessed the chloride in fly ash using X-ray diffraction (XRD) analysis and successfully specified  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{CaCl}_2$ , and  $\text{CaClOH}$  <sup>6,7,9</sup>.

In this chapter, I will use the method of combining X-ray absorption near edge structure (XANES) with X-ray diffraction (XRD) to find out the mechanism in scientific way. Firstly, I will analyze the chloride speciation in the three kinds of fly ashes, RFA, CaFA and NaFA. Then, I will discuss the chloride behavior in the washing experiments.

### **3.2 Experiment material and method**

### 3.2.1 Experiment material

Three kinds of fly ashes were used: RFA, CaFA and NaFA. They are the same material I used in the washing experiments. Here, I checked the chlorine content in those fly ashes again by ion chromatography (DX-AQ AI-450, DIONEX Co., Ltd., Japan) and the composition of those fly ashes is shown in Table 3.1. When I discuss the chloride speciation in three kinds of fly ashes or chloride behavior in washing process, I will introduce other corresponding samples in detail in corresponding content.

Table 3.1 Element content of RFA, CaFA and NaFA (weight %)

Element	RFA	CaFA	NaFA	Element	RFA	CaFA	NaFA	Element	RFA	CaFA	NaFA
<b>O</b>	37.3	24.6	13.2	<b>K</b>	2.99	3.38	5.84	<b>Fe</b>	2.32	1.24	0.713
<b>Si</b>	4.97	2.68	1.28	<b>Na</b>	2.97	3.46	18.5	<b>Zn</b>	0.223	0.390	0.893
<b>C</b>	3.24	7.55	8.17	<b>Ti</b>	1.51	0.821	0.535	<b>Cu</b>	0.238	0.0639	0.147
<b>Cl</b>	6.81	16.2	33.9	<b>Mg</b>	1.12	0.722	0.341	<b>Pb</b>	0.387	0.212	1.23
<b>S</b>	3.31	1.81	1.31	<b>P</b>	0.666	0.241	0.179	<b>Br</b>	0.111	0.269	0.914
<b>Ca</b>	24.7	28.2	10.2	<b>Al</b>	3.99	4.30	5.92				

### 3.2.2 Experiment method

The main analytical methods used are XRD and XANES. The crystal chlorides were identified using XRD (RINT-Ultima+/PCQ2, Rigaku, Japan).

The XRD method is now widely used for identification of crystals, following the basic theory of the Bragg equation:

$$2d\sin\theta = n\lambda \quad (3.1)$$

where  $d$  is the special distance between the crystal lattice,  $\theta$  is the angle of incidence,  $\lambda$  is the wavelength of the incidence wave, and  $n = 1, 2, 3, 4, \dots$

When the incidence wave is fixed, as in a crystal, a special distance between the crystal lattice is in accordance with the angle of incidence, at which direction the energy of the ray will be strengthened. Thus, with the checked angle, it can be deduced can deduce the special lattice distance, as well as the kind of crystal. XRD data are also presented as basic information for XANES data analysis.

### XANES

The XANES experiments were carried out at beam-lines BL-9A and BL-11B at the Photon Factory, a synchrotron radiation facility in Tsukuba, Japan. The energy range of BL-9A is 2.1–15 keV [Si (111)] and that of BL-11B is 2.02–3.911 keV [Ge (111)]<sup>10, 11</sup>. The spectral data were collected as fluorescence yield (FY) and total electron yield (TEY) in BL-11B and conversion electron yield (CEY) in BL-9A.

The linear combination fit (LCF) technique of XANES spectra has been successfully applied in environmental fields for quantitative speciation analysis of some identical mixtures<sup>12, 13</sup>. The method compares the spectra of samples to the spectra of a series of reference compounds. I conducted LCF using the commercial software REX 2000 version 2.3 (Rigaku Co. Ltd., Japan). The residual value (R) calculated by Formula. (3.2) was used to evaluate the results deduced from the LCF method.

$$R = \frac{\sum (XANES_{Measured} - XANES_{Calculated})^2}{\sum (XANES_{Measured})^2} \quad (3.2)$$

### 3.3 Chloride speciation analysis in three kinds of fly ashes

#### 3.3.1 Research contents and purposes

In this section I will accomplish the following two tasks. One is to identify what kind of chlorides exists in the three kinds of fly ashes, and the other is to determine the portion of chlorine in the corresponding form.

Some researchers have identified the existence of some chlorides in fly ashes by XRD<sup>6, 7, 9</sup>, however, XRD is difficult to determine, among all the chlorides, how much chlorine is in NaCl form, how much chlorine is in KCl form, and moreover, XRD can not distinguish amorphous chlorides, which are thought to be in fly ashes. So in addition to XRD I utilize another method, XANES, which is effective for both crystal and amorphous compound, and is possible to get the information of distribution of each kind of chlorides.

#### 3.3.2 Additional samples and Methods

##### 3.3.2.1 Additional samples

Except the three kinds of fly ashes, three other samples, i.e., RFAT1, CaFAT1 and NaFAT1, were obtained from single-washing experiments, the procedures of which are described in Figure 3.1. The washing conditions are L/S of 3, a mixing speed of 150 rpm, and a mixing time of 5 min. In Chapter 2 I found that under the condition of a fixed mixing time of 5 min and mixing speed of 150 rpm, an L/S ratio of 3 was the turning point in chlorine reduction in single-washing experiments for these three kinds of fly ashes <sup>8</sup>. RFAT1, CaFAT1, and NaFAT1 are the solids that were produced by drying the washing solution from the RFA, CaFA, and NaFA single-washing experiments (L/S = 3), respectively. The samples were dried at 105°C for 24 h.

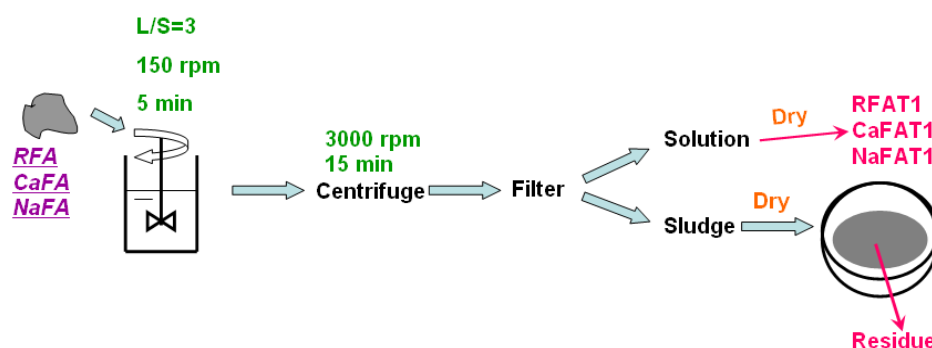


Figure 3.1 The procedure of single-washing experiment

### 3.3.2.2 Identification approach

First, reference chlorides were chosen based on the element content of the three fly ashes and a literature review. Second, by comparing the chlorine K-edge XANES spectra of fly ashes and those of reference chlorides and by examining the washing experiment results, I excluded some chlorides from LCF analysis to produce a list of “possible reference chlorides.”

After verifying the reliability of LCF method in this research, I discussed the chloride chemical form found in RFA, CaFA, and NaFA separately. I first examined the XRD spectra of fly ash and samples from the washing experiment. Based on the relationship among RFA, CaFA, and NaFA, I then separated the “possible reference chlorides” into three groups: A) chlorides that must be in fly ash, identified by the XRD spectra of fly ash; B) chlorides that have a high possibility of being in fly ash, as determined by XRD spectra of samples from washing experiments; and C) chlorides less likely to be in fly ash, i.e., the remaining chlorides.

Lastly, I finalized the “A” group chlorides and selected one or two additional chlorides

from the “B+C” group for LCF analysis. I chose the combination with the lowest R value and used the results from previous research to verify that combination as well as the corresponding distribution of chlorides. The diagram of the analysis procedure is delineated in Figure 3.2.

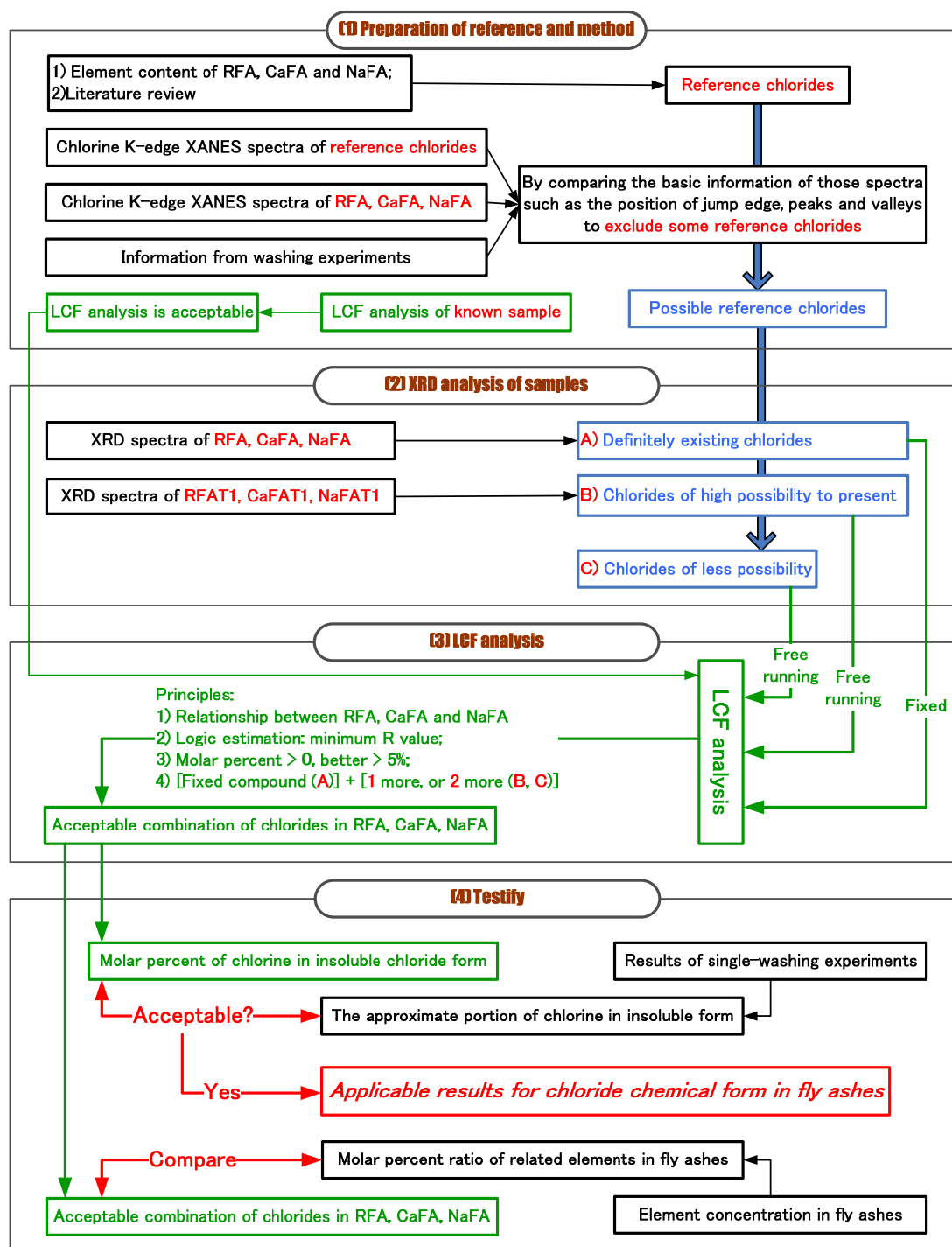


Figure 3.2 Analysis procedure speciation analysis of chlorides in RFA, CaFA and NaFA

### 3.3.2.3 XANES spectra of the reference chlorides

According to the element contents of RFA, CaFA, and NaFA in Table 3.1 and previous studies <sup>7, 9, 14</sup>, KCl, NaCl, CuCl<sub>2</sub>, FeCl<sub>3</sub>, MgCl<sub>2</sub>, PbCl<sub>2</sub>, ZnCl<sub>2</sub>, AlCl<sub>3</sub>•6H<sub>2</sub>O, FeCl<sub>2</sub>•4H<sub>2</sub>O, Friedel's salt ([Ca<sub>2</sub>Al(OH)<sub>6</sub>]Cl•2H<sub>2</sub>O), and calcium hydroxychloride (CaClOH) are chosen as the reference chlorides. When Friedel's salt is heated up to 670°C, calcium chloroaluminate (11CaO•7Al<sub>2</sub>O<sub>3</sub>•CaCl<sub>2</sub>) is formed <sup>15</sup>. Thus, calcium chloroaluminate is also included in the reference chlorides.

Friedel's salt, calcium chloroaluminate, and calcium hydroxychloride were self made and checked using XRD <sup>15, 16, 17</sup>, and the detailed procedure is shown in "Appendix No. 2." Other reference chlorides were purchased from Nacalai Tesque (Kyoto, Japan), Soegawa Rikagaku (Tokyo, Japan), or Nichika Corp (Kyoto, Japan). The Cl K-edge XANES spectra of reference chlorides are shown in Figure 3.3.

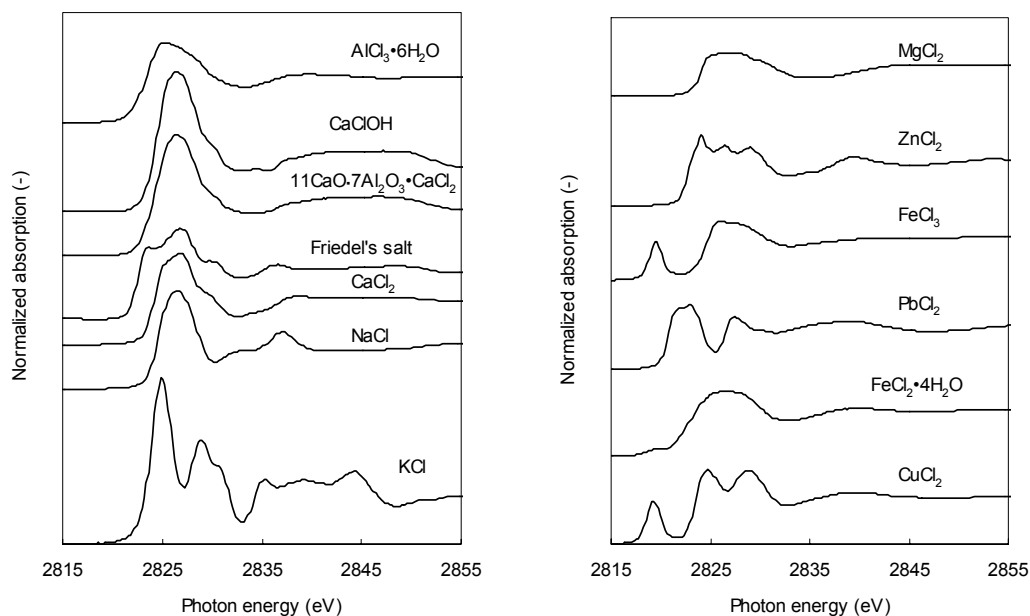


Figure 3.3 Chlorine K-edge XANES spectra of reference chlorides

## 3.3.3 Results and discussion

### 3.3.3.1 XANES spectra of RFA, CaFA and NaFA

Figure 3.4 shows the chlorine K-edge XANES spectra of RFA, CaFA, and NaFA. The

spectra of the three fly ashes share some similar characteristics. The first peak is positioned near 2,826 eV, followed by a small second peak at approximately 2,837 eV, which is very obvious in NaFA, but not so obvious in RFA and CaFA.

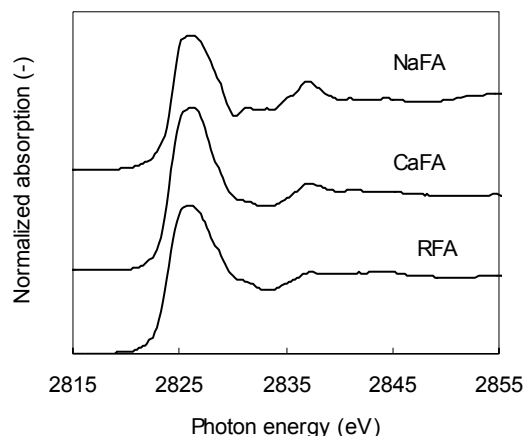


Figure 3.4 Chlorine K-edge XANES spectra of RFA, CaFA, and NaFA

Comparison to the chlorine K-edge XANES spectra of the reference chlorides (See Figure 3.3) indicates that  $\text{FeCl}_3$  and  $\text{CuCl}_2$  either are not present or are present at very low levels in the three fly ashes because the pre-edge peak positions of the  $\text{FeCl}_3$  and  $\text{CuCl}_2$  spectra are located before 2,822 eV. The presence of a valley in the spectral profile of  $\text{PbCl}_2$  at around 2,826 eV, rather than a peak, indicates that the concentration of  $\text{PbCl}_2$  is likely very low; therefore, I exclude  $\text{PbCl}_2$ .  $\text{ZnCl}_2$  is excluded with the same reason. Considering incineration operating conditions of MSW, the presence of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  is unlikely. Because the concentration of magnesium is not very high, magnesium chloride is also unlikely to be a considerable component of the chlorides in fly ash.  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  is soluble in water. In the solution from the washing experiments, Na, K, and Ca were detected by ICP-AES at considerable concentrations, whereas Al was detected at very low concentrations. As a result,  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  is also excluded. Therefore, the “possible reference chlorides” are NaCl, KCl,  $\text{CaCl}_2$ ,  $[\text{Ca}_2\text{Al}(\text{OH})_6]\text{Cl} \cdot 2\text{H}_2\text{O}$ ,  $11\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \cdot \text{CaCl}_2$ , and  $\text{CaClOH}$ . For convenience,  $11\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \cdot \text{CaCl}_2$  is hereafter described as “F670.”

### 3.3.3.2 LCF analysis of a known sample

I prepared a mixture of RFA and  $\text{CaCl}_2$ , referred to as RCA, to evaluate the



applicability of LCF analysis. RCA contains 23% chlorine from RFA and 77% chlorine from  $\text{CaCl}_2$ . LCF analysis was applied to the chlorine K-edge XANES spectrum of RCA, and the results indicated that 21% of the chlorine was from RFA and 79% from  $\text{CaCl}_2$ , with an R value of 0.036 (see Figure 3.5). This result confirms that LCF analysis can be applied well in my research.

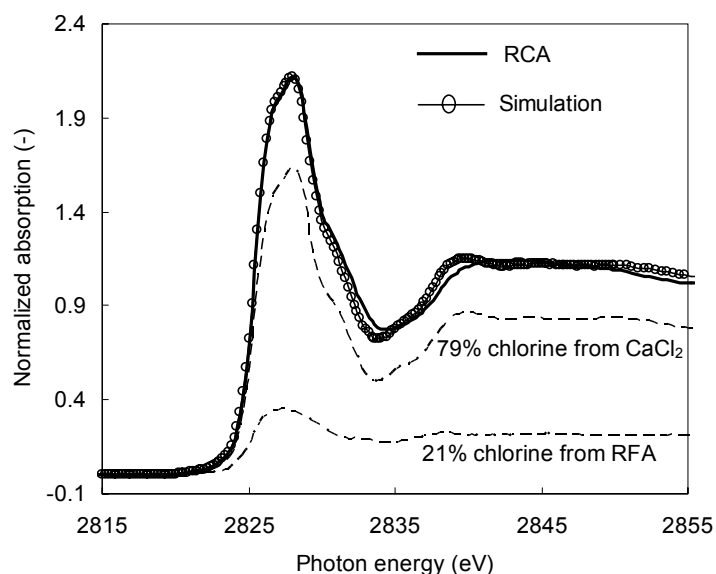
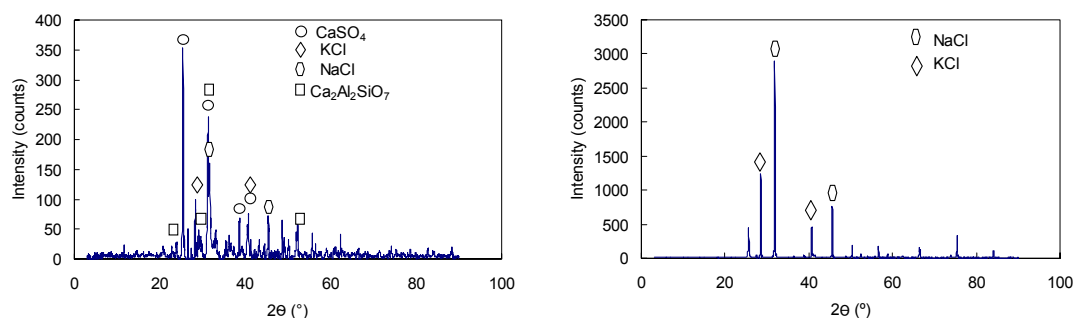


Figure 3.5 LCF analysis of chlorine K-edge XANES spectrum of RCA

### 3.3.3.3 Chemical forms of chloride in RFA

The XRD analysis of RFA and RFAT1 confirms the existence of  $\text{KCl}$  and  $\text{NaCl}$  in RFA (See Figure 3.6a and b). Thus,  $\text{NaCl}$  and  $\text{KCl}$  belong in the “A” group of chlorides for RFA. The chlorides of the “C” group are  $\text{CaCl}_2$ , Friedel’s salt, F670, and  $\text{CaClOH}$ . I then process the LCF analysis of Cl K-edge XANES spectra for RFA by fixing  $\text{NaCl}$  and  $\text{KCl}$  and including one or two chlorides from the “C” group (See Table 3.2). First, I add one more compound to try three-compound combinations from #2 to #5. Among the three-compound combinations, combination #2 has the lowest R value, indicating the high possibility that  $\text{CaCl}_2$  is present in RFA. Given the presence of  $\text{NaCl}$ ,  $\text{KCl}$ , and  $\text{CaCl}_2$ , one more compound is added to process four-compound combinations. Because the content of  $\text{CaClOH}$  is negative in the combination “ $\text{NaCl} + \text{KCl} + \text{CaCl}_2 + \text{CaClOH}$ ,” only combinations #6 and #7 are possible. Of these two combinations, #6 is more promising, with a lower R value; therefore, Friedel’s salt is thought to be present

in RFA. Therefore, the chloride in RFA is composed of 15% NaCl, 10% KCl, 50% CaCl<sub>2</sub>, and 25% Friedel's salt.



a) XRD analysis of RFA

b) XRD analysis of RFAT1

Figure 3.6 XRD analysis of RFA and RFAT1

Table 3.2 Calculated molar percentage of chlorine in different chlorides form among all the chlorine in RFA (molar %)

	NaCl	KCl	CaCl <sub>2</sub>	Friedel	F670	CaClOH	R
#1	68	32					0.12
#2	14	13	73				0.067
#3	43	17		40			0.071
#4	27	19			54		0.077
#5	46	27				26	0.10
#6	15	10	50	25			0.046
#7	13	14	57		16		0.065

According to our previous research <sup>8</sup>, approximately 78% of chlorine in RFA was soluble. In combination #6, the soluble chloride is “NaCl + KCl + CaCl<sub>2</sub>,” and the total molar percentage of chlorine in these forms is 75%. The two results are very similar. When I checked RFAT1 by XRD, it was found to be very hygroscopic, suggesting the presence of CaCl<sub>2</sub>. The typical XRD peak of Friedel's salt is located around  $2\theta = 11.3^\circ$ ; in the XRD results for RFA, an obvious small peak was found around that area. As a result, it is reasonable to conclude that among all of the chlorine in RFA, 15% is present as NaCl, 10% as KCl, 50% as CaCl<sub>2</sub>, and the remainder as Friedel's salt.

I would compare the molar percentage ratio of related elements in all chlorides with that in RFA. Based on combination #6 (15% NaCl + 10% KCl + 50% CaCl<sub>2</sub> + 25% Friedel's salt), the element molar ratio of Na, K, Ca, and Al in all chlorides is as

follows in Formula (3.3).

$$m_{Ca,Cl} : m_{Al,Cl} : m_{Na,Cl} : m_{K,Cl} = 60 : 20 : 12 : 7.7 \quad (3.3)$$

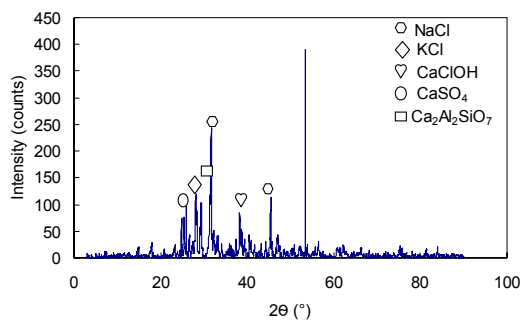
Based on the element content data from Table 3.1, the molar percentage ratio of Ca, Al, Na, and K in RFA is presented in Formula (3.4).

$$m_{Ca,P} : m_{Al,P} : m_{Na,P} : m_{K,P} = 64 : 15 : 13 : 7.9 \quad (3.4)$$

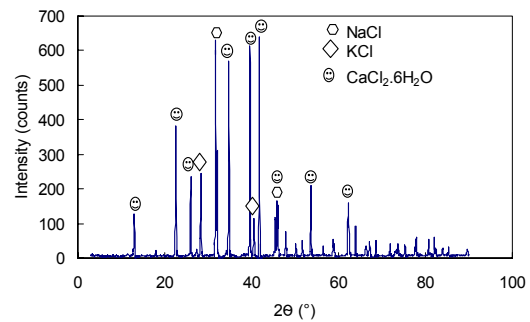
The calculation process for Formulas (3.3) and (3.4) is available in “Appendix No. 3.” The calculated molar ratio of Ca, Al, Na, and K among the reference chlorides and the practical molar ratio of Ca, Al, Na, and K in RFA are comparable, which suggests that most of these elements are related to chlorides.

### 3.3.3.4 Chemical forms of chloride in CaFA

The XRD results of CaFA and CaFAT1 show that NaCl, KCl, and CaClOH must be present in CaFA and therefore account for the CaFA “A” group of chlorides (See Figure 3.7a and b). There is a high possibility that  $CaCl_2$  exists in CaFA; thus it falls into the “B” group for CaFA. Given the relationship between RFA and CaFA and the limited possibility that F670 is present in RFA, F670 is excluded. Therefore, only Friedel’s salt is in the “C” group. The LCF analysis of CaFA proceeds in a similar manner as for RFA (See Table 3.3). Combination #4 has the lowest R value of 0.033, indicating that among the chloride in CaFA, 35% is present as NaCl, 11% as KCl, 37% as  $CaCl_2$ , 13% as Friedel’s salt, and the remaining 4% as CaClOH.



a) XRD analysis of CaFA



b) XRD analysis of CaFAT1

Figure 3.7 XRD analysis of CaFA and CaFAT1

Table 3.3 Calculated molar percentage of chlorine in different chlorides form among all the chlorine in CaFA (molar %)

	NaCl	KCl	CaClOH	CaCl <sub>2</sub>	Friedel	R
#1	54	22	24			0.065
#2	33	13	2	52		0.042
#3	46	15	18		21	0.045
#4	35	11	4	37	13	0.033

Our previous research indicates that approximately 83% of the chloride in CaFA is soluble chloride <sup>8</sup>. The data for combination #4 indicate a soluble portion of 87% (NaCl + KCl + CaCl<sub>2</sub> + CaClOH). Thus, the washing experiment and the LCF results are in good agreement. It is reasonable to conclude that of the total chlorine in CaFA, 35% is in the form of NaCl, 11% is KCl, 37% is CaCl<sub>2</sub>, 13% is Friedel's salt, and the remaining 4% is in the form of CaClOH.

The molar percentage ratio of Ca, Al, Na, and K in all chlorides in CaFA is presented in Formula (3.5):

$$m_{Ca,Cl} : m_{Al,Cl} : m_{Na,Cl} : m_{K,Cl} = 45 : 12 : 32 : 10 \quad (3.5)$$

Whereas the molar percentage ratio of Ca, Al, Na, and K in CaFA is as follows in Formula (3.6):

$$m_{Ca,P} : m_{Al,P} : m_{Na,P} : m_{K,P} = 64 : 15 : 14 : 7.9 \quad (3.6)$$

The calculation process is similar as that of RFA analysis. Considering the excess injection of Ca(OH)<sub>2</sub> in CaFA, it is understandable that the total calcium portion is higher than that in the cations of all chlorides. For sodium, the data are different.

### 3.3.3.5 Chemical forms of chloride in NaFA

The XRD spectra for NaFA and NaFAT1 indicate the existence of NaCl and KCl, the “A” group chlorides for NaFA (See Figure 3.8a and b). Considering the low portion of CaClOH in CaFA and the different formation of NaFA from CaFA, CaClOH is excluded from the LCF analysis of NaFA. F670 is also excluded for the same reason as in CaFA. Thus, CaCl<sub>2</sub> and Friedel's salt are the “C” group chlorides for NaFA. Because there must be insoluble chlorides in NaFA, Friedel's salt is included. The LCF results are presented in Table 3.4. With the combination “NaCl + KCl + CaCl<sub>2</sub> + Friedel's

salt,” the molar percent of  $\text{CaCl}_2$  is negative, so the result is not shown. With a lower R value, combination #2 is clearly better than combination #1. For all of the chlorine in NaFA, 79% is in the form of NaCl, 12% is KCl, and 9% is in the form of Friedel’s salt. Our previous research indicated that approximately 5.5% of chlorine in NaFA is not easily soluble <sup>8</sup>, which is close to the 9% of chlorine in the form of Friedel’s salt, as determined by LCF analysis. Considering the relationship between RFA and NaFA, there might be some  $\text{CaCl}_2$ , but possibly the portion of it is too little to be checked out. Thus, approximately 79% of the total chlorine is in the form of NaCl, approximately 12% is KCl, and approximately 9% is in the form of Friedel’s salt.

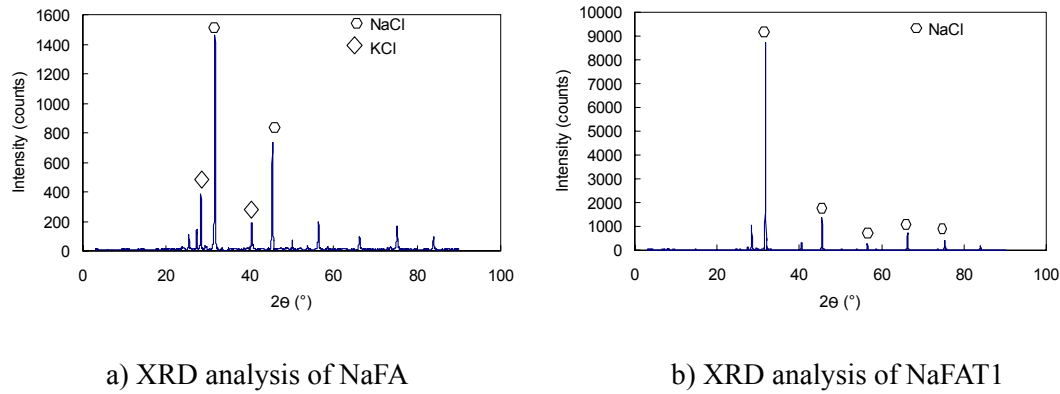


Figure 3.8 XRD analysis of NaFA and NaFAT1

Table 3.4 Calculated molar percentage of chlorine in different chlorides form among all the chlorine in NaFA (molar %)

	NaCl	KCl	Friedel	R
#1	83	17		0.032
#2	79	12	9	0.028

As with RFA and CaFA, I calculate the molar percentage ratio of Ca, Al, Na, and K in all chlorides as shown in Formula (3.7):

$$m_{\text{Ca,Cl}} : m_{\text{Al,Cl}} : m_{\text{Na,Cl}} : m_{\text{K,Cl}} = 15 : 7.4 : 68 : 10 \quad (3.6)$$

The molar percentage ratio of Ca, Al, Na, and K in NaFA is as follows in Formula (3.8):

$$m_{\text{Ca,P}} : m_{\text{Al,P}} : m_{\text{Na,P}} : m_{\text{K,P}} = 18 : 15 : 56 : 11 \quad (3.8)$$

The calculation processes is similar as that of RFA analysis or CaFA analysis. The two

ratios are comparable, except for Al, which accounted for more than twice the proportion of chloride in the NaFA ratio than in the all-chlorides ratio.

### **3.3.4 Brief summary and comments**

Other research <sup>18</sup> has shown that the neutralizing capacity of  $\text{Ca}(\text{OH})_2$  powder is much lower than that of  $\text{NaHCO}_3$  powder for acid gas removal in flue gas in municipal solid waste incinerators. Therefore, the injection of  $\text{NaHCO}_3$  is more favorable in the mass reduction of fly ash. It can be deduced that more newly formed insoluble chlorides are present in CaFA than in NaFA, suggesting that  $\text{NaHCO}_3$  is superior to  $\text{Ca}(\text{OH})_2$  as an alkaline reagent from the viewpoint of both chloride reduction and the chemical form of chloride. Recently, various fly ash recycling processes, besides the reuse of fly ash as a raw material in cement, have been proposed <sup>19</sup>. My research provides basic information that can be used to develop more effective processes.

I determined the chloride chemical form and the corresponding quantitative speciation of chlorides in fly ash using a combination of XANES (XAFS) and XRD methods. However, I used Friedel's salt to represent all insoluble chlorides in fly ash, which is not a comprehensive method, considering the complex conditions in incinerators and the various compounds present in municipal solid waste. More insoluble chlorides should be considered. Except for the presence of the typical peak of Friedel's salt in RFA XRD spectra, only the R value from LCF analysis provided strong evidence of its presence. As a result, further experiments based on the characteristics of Friedel's salt should be carried out to confirm its presence. For example, fly ash can also be washed by injecting  $\text{CO}_2$  or after aging, heating, or adjusting the pH, and these results should be compared with those from the normal washing experiment. With respect to the XANES and LCF analysis methods, the reference spectra are very important to the LCF results. If the sample and reference spectra are measured on the same day in the same beam line, the processed LCF results are more reliable. Also, it is necessary to obtain and compare both FY and TEY sample data.

## **3.4 Comparison of chloride behavior in washing experiments between CaFA and NaFA**

### **3.4.1 Research contents and purposes**

Since I have got the information of chloride speciation in three kinds of fly ash, I am going to analyze the chloride behavior in the washing experiments of those fly ashes. And because it needs to compare the superiority of the alkaline reagent, I have to discuss the chloride behavior in washing experiments of CaFA and NaFA together. To find out the chloride behavior in washing experiments has another purpose, which is to optimize the parameters of washing process.

### **3.4.2 Additional samples and Methods**

#### **3.4.2.1 Additional samples**

Based on the results of the washing experiments, I selected some residue samples, which are taken from the critical washing experiments. I analyzed them by XANES and XRD. The detailed contents of those residues are outlined in Table 3.5. In single-washing experiments, I found that the L/S ratio is more important than mixing time or mixing speed to reduce residue mass percentage and chlorine content. Thus, in single-washing experiments, I fixed the mixing time at 5 min and the mixing speed at 150 rpm. I also found that an L/S ratio of 3 is a threshold; when the L/S ratio is larger than 3, the residue mass percentage and chloride content in the residue decrease much slower than the increasing speed of the L/S ratio. An L/S ratio of 10 is the maximum L/S ratio in the single-washing experiments<sup>8</sup>. Because NaFA contains more soluble chloride than CaFA does<sup>20</sup>, the movement of chloride may be more obvious at the region with smaller L/S ratio than at the region with higher L/S ratio in single-washing experiments. Thus, for NaFA I selected the single-washing residue with an L/S ratio of 5, and for CaFA I chose the single-washing residue with an L/S ratio of 6. I also selected one residue sample from the double-washing experiment to evaluate the effect of washing frequency on the washing process, which is accordant to the 17# experiment condition in Chapter 2 (Refer to Table 2.7). The original fly ash, CaFA and NaFA, are named as CaFA-0# and NaFA-0# respectively.

Table 3.5 Samples from washing experiments

Code	Washing experiment	L/S ratio	Mixing time	Mixing speed	Fly ash
3#	Single-washing	3	5 min	150 rpm	Both
5#		5	5 min	150 rpm	NaFA
6#		6	5 min	150 rpm	CaFA
8#		10	5 min	150 rpm	Both
II#	Double-washing	1 <sup>st</sup> step	3	5 min	Both
		2 <sup>nd</sup> step	3	10 min	

Additional samples (CaFAT1, CaFAT2, NaFAT1, and NaFAT2) were prepared from the washing experiments. CaFAT1 is the dried solids from the washing solution of the first step of the double-washing of CaFA. The drying condition is 105°C for 24 hr. CaFAT2 is the dried solids from the washing solution of the second step of the double-washing of CaFA. NaFAT1 and NaFAT2 are the corresponding materials for NaFA. The detailed procedures are included in Figure 3.9. CaFAT1, CaFAT2, NaFAT1, and NaFAT2 are also examined by XRD and XANES. CaFAT1 and NaFAT1 are just the same sample “CaFAT1, NaFAT2” which I used in the section 3.3.

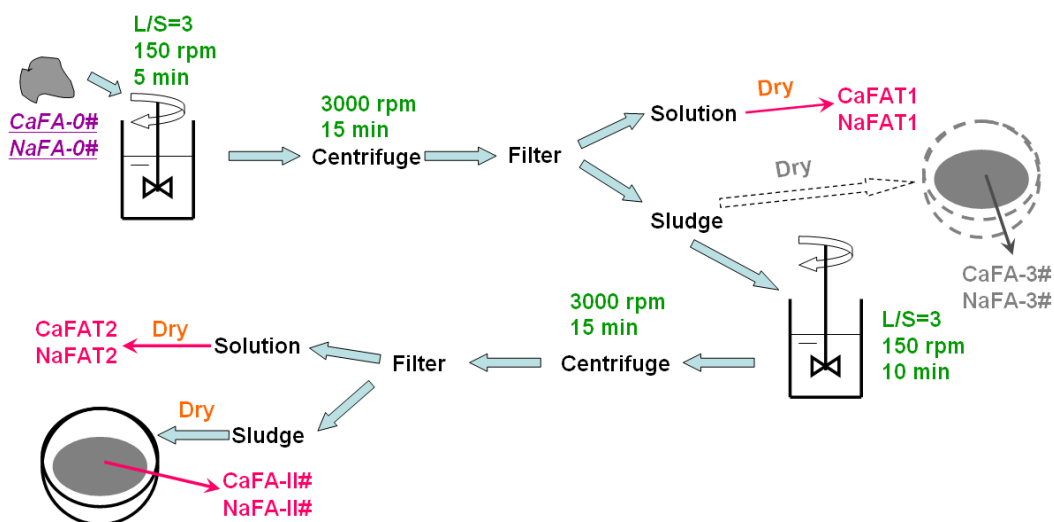


Figure 3.9 Procedure of CaFA and NaFA double-washing experiments

### 3.4.2.2 Methods

I used the method of combining XANES with XRD to determine the chemical forms in three kinds of fly ash and the chloride behavior in washing experiments<sup>8</sup>. First, based on the element concentrations shown in Table 2.1, our previous research<sup>20</sup>, and results



of a literature review, I chose the possible reference chlorides. Second, based on XRD spectra of samples, I confirmed the existence of some chlorides in residues, which I called “A” group chlorides; the remaining chlorides were classified as “B” group chlorides, which might be present in residues. I then fixed the “A” group chlorides and added one, two, or even three more chlorides from the “B” group for the linear combination fit analysis, as discussed below. The combination that produced the minimum R value is chosen. XRD was used to confirm the existence of crystal chlorides in washed residues of fly ash.

### 3.4.2.3 XANES spectra of the reference chlorides

In previous section or research <sup>20</sup>, I found that in CaFA, 35% of chlorine presented as NaCl, 11% as KCl, 37% as CaCl<sub>2</sub>, 13% as Friedel’s salt, and the remaining 4% as CaClOH, whereas in NaFA, about 79% of chlorine was in NaCl, 12% was in KCl, and 9% was in Friedel’s salt. Therefore, I choose the following chlorides: NaCl, KCl, CaCl<sub>2</sub>, CaCl<sub>2</sub>•2H<sub>2</sub>O, [Ca<sub>2</sub>Al(OH)<sub>6</sub>]Cl•2H<sub>2</sub>O, 11CaO•7Al<sub>2</sub>O<sub>3</sub>•CaCl<sub>2</sub>, and CaClOH. CaCl<sub>2</sub>•2H<sub>2</sub>O refers to the hydrates formed from CaCl<sub>2</sub> during the washing experiments. [Ca<sub>2</sub>Al(OH)<sub>6</sub>]Cl•2H<sub>2</sub>O is Friedel’s salt, which, when heated, will gradually change to calcium chloroaluminate (11CaO•7Al<sub>2</sub>O<sub>3</sub>•CaCl<sub>2</sub>) at 670°C. Because all washed residues were dried at 105°C for 24 hr, 11CaO•7Al<sub>2</sub>O<sub>3</sub>•CaCl<sub>2</sub> is included in the research. For convenience, I use “F670” to represent 11CaO•7Al<sub>2</sub>O<sub>3</sub>•CaCl<sub>2</sub> in the following content. Figure 3.10 shows the Cl K-edge XANES spectra of the reference chlorides. Friedel’s salt, F670, and calcium hydroxychloride (CaClOH) were composed and checked by XRD <sup>15, 16</sup>, and other reference chlorides were purchased from Nacalai Tesque (Kyoto, Japan), Soegawa Rikagaku (Tokyo, Japan), or Nichika Corp. (Kyoto, Japan).

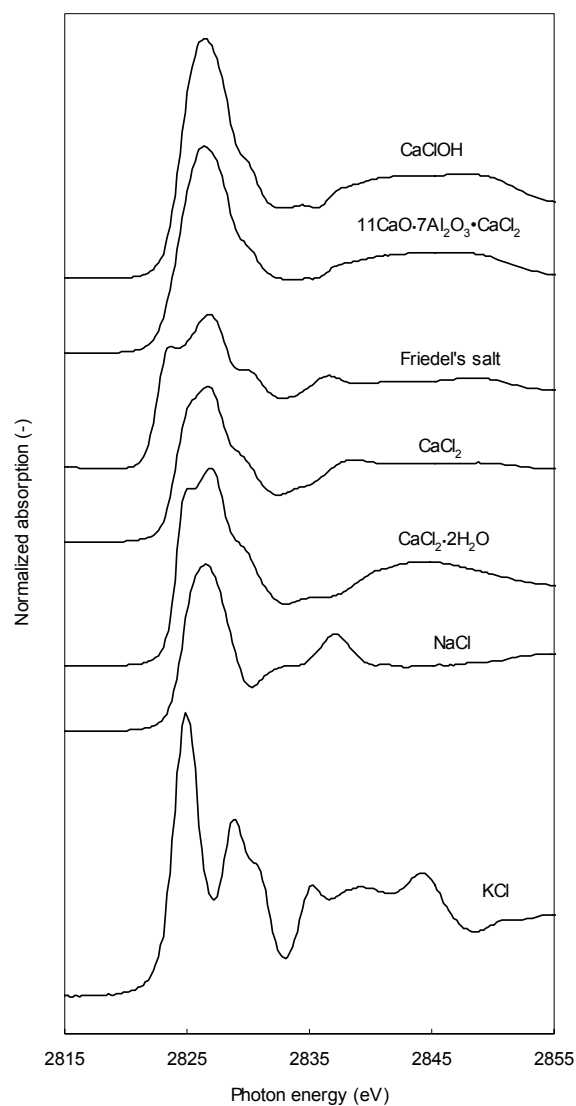


Figure 3.10 Chlorine K-edge XANES spectra of reference chlorides

### 3.4.3 Results and discussions

#### 3.4.3.1 LCF analysis of CaFA samples with XRD results

Table 3.6 lists the element concentrations in CaFA-3#, CaFA-6#, CaFA-8#, and CaFA-II# (“-3#”, “-4#”, “8#” and “-II#” mean the corresponding experiment code showed in Table 3.5), and the corresponding residue weight percentages. The residue weight percent is the ratio of the amount of remaining dried washed residue to the amount of fly ash that was used in the washing experiments. Although the residue mass

percent of CaFA-8# is less than that of CaFA-II#, the total amount of chlorine left in the residue of CaFA-8# is larger than that in the residue of CaFA-II#. The chlorine concentrations in CaFAT1 and CaFAT2 are 3.77% and 1.34%, respectively.

Table 3.6 Element concentration and residue weight percentage of CaFA-3#, CaFA-6#, CaFA-8#, and CaFA-II# (weight %)

Samples	Cl	Ca	Na	K	Al	S	Si	Residue weight percent
CaFA-3#	7.19	26.2	0.972	1.54	2.03	2.22	3.88	85.5
CaFA-6#	4.47	26.5	0.790	1.22	2.13	2.09	4.11	79.2
CaFA-8#	3.61	27.2	0.790	1.03	2.08	2.13	4.11	76.0
CaFA-II#	2.67	26.0	0.694	0.87	2.17	2.33	4.23	76.9

Figure 3.11 presents the XRD spectra of the samples in Table 3.6, CaFAT1 and CaFAT2. It confirms that NaCl, KCl, and some kind of  $\text{CaCl}_2$  hydrates exist in all single-washing experiment residues. As I only have the chlorine K-edge XANES spectrum of  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ , I use  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  to represent the hydrates in the residues. NaCl and KCl must exist in the residue of CaFA-II#. With this information, I begin LCF analysis of those samples. Figure 3.12 shows the chlorine K-edge XANES spectra of CaFA-0#, CaFA-3#, CaFA-6#, CaFA-8#, CaFA-II#, CaFAT1, and CaFAT2. The spectra of residues have similar shapes; the first peak is around 2,826 eV, followed by a valley. But there are more fine structures in the CaFA-0# spectrum than in the spectra of other residues. The spectra of CaFAT1 and CaFAT2 are very similar to that of  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ , suggesting that most of the chlorides in CaFAT1 or CaFAT2 may be in the form of  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ .

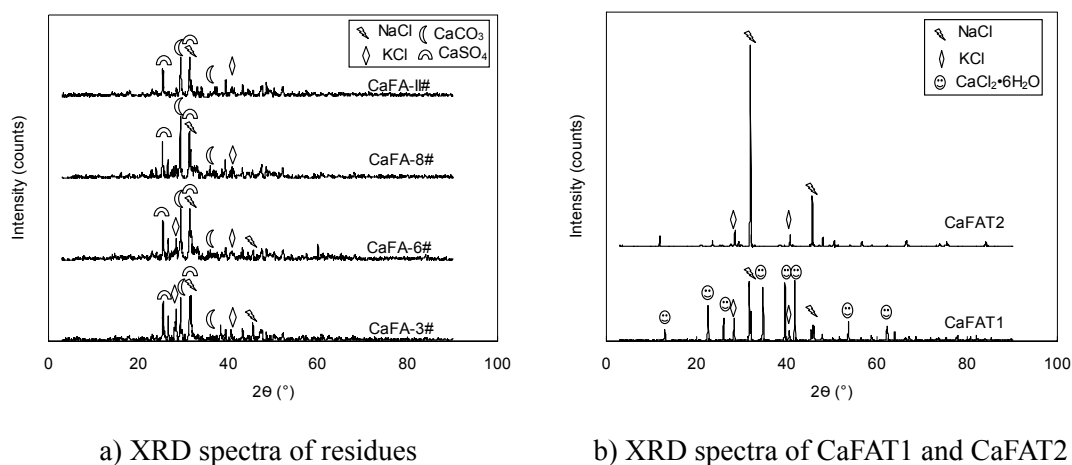
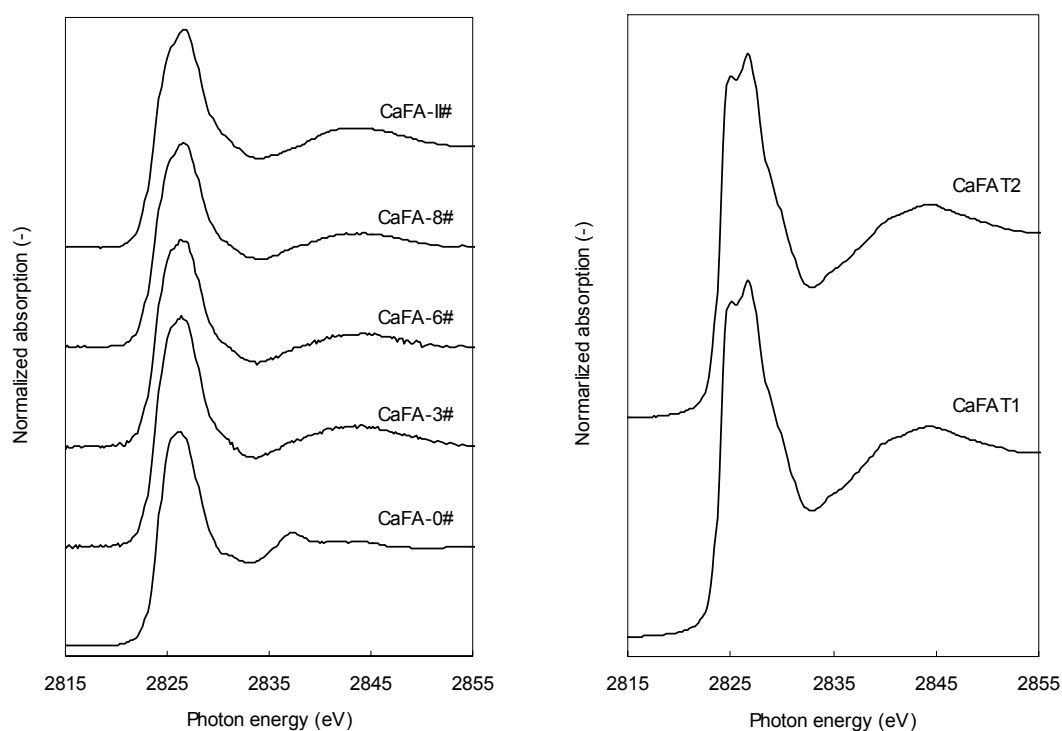


Figure 3.11 XRD spectra of CaFA-3#, 6#, 8#, and II# and CaFAT1 and CaFAT2



a) XANES spectra of residues

b) XANES spectra of CaFAT1 and CaFAT2

Figure 3.12 Chlorine K-edge XANES spectra of CaFA washing samples

Here, I will examine in detail the results of the LCF analysis of CaFA-3# residue, as an example. Based on the above analysis, I conclude that NaCl, KCl, and  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  must exist in the residue of CaFA-3#, and CaClOH, Friedel's salt, and F670 may be present. Thus, the "A" group chlorides for CaFA-3# are NaCl, KCl, and  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ , and the "B" group chlorides are CaClOH, Friedel's salt, and F670. Therefore, I fix NaCl, KCl, and  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  and add one more compound from the "B" group chlorides to process a four-compound combination in the LCF analysis. The results are combinations [2] and [3] in Table 3.7. The resulting value of the portion of CaClOH in the combination "NaCl + KCl +  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  + CaClOH" is negative, so the result for that combination is not shown, as with the other combinations including CaClOH. Combination [2] has a smaller R value than combination [3], suggesting that Friedel's salt is more likely than F670 to be found in the residue of CaFA-3#. Finally, I examine NaCl, KCl,  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ , Friedel's salt, and F670 as a five-compound combination, i.e., combination [4] in Table 3.7. Combination [4] has the lowest R value; therefore, I choose combination [4] as the possible combination for CaFA-3#.

Table 3.7 The LCF analysis of chlorine K-edge XANES spectrum of CaFA-3# (%)

<b>Combinations</b>	<b>NaCl</b>	<b>KCl</b>	<b>CaCl<sub>2</sub>•2H<sub>2</sub>O</b>	<b>CaClOH</b>	<b>Friedel</b>	<b>F670</b>	<b>R</b>
[1]	27	11	62				0.069
[2]	19	5	49		27		0.034
[3]	13	13	18			56	0.054
[4]	16	6	39		24	15	0.033

The LCF analysis of CaFA-6#, CaFA-8#, CaFA-II#, CaFAT1, and CaFAT2 followed a similar procedure as outlined above, and the results are listed in Table 3.8. Because CaFA-0# was obtained from a bag filter and preserved in a sealed bottle, I used CaCl<sub>2</sub> in the combination for CaFA-0#. According to the data in Table 3.8, CaClOH cannot be examined in the washed residue, CaFAT1 and CaFAT2. This may be because its concentration is too low to be detected; alternatively, during the washing process it may have changed into CaCl<sub>2</sub>•2H<sub>2</sub>O, considering that CaClOH is one of the product of the “Ca(OH)<sub>2</sub> + CaCl<sub>2</sub>” system according to the molar ratio of Ca(OH)<sub>2</sub> to CaCl<sub>2</sub>. If I included Friedel’s salt and F670 together as “insoluble chlorides,” the portion of insoluble chlorides increases as the L/S ratio or washing frequency increases. Regarding the portion of chlorine in CaCl<sub>2</sub>•2H<sub>2</sub>O form, there is little variation among the residues, whereas the portion of chlorine in NaCl and KCl forms gradually decreases from CaFA-0# to CaFA-II#. These results are discussed below, together with the corresponding results of NaFA.

Table 3.8 LCF analysis of CaFA-0#, CaFA-3#, CaFA-6#, CaFA-8#, CaFA-II#, CaFAT1, and CaFAT2 (molar %)

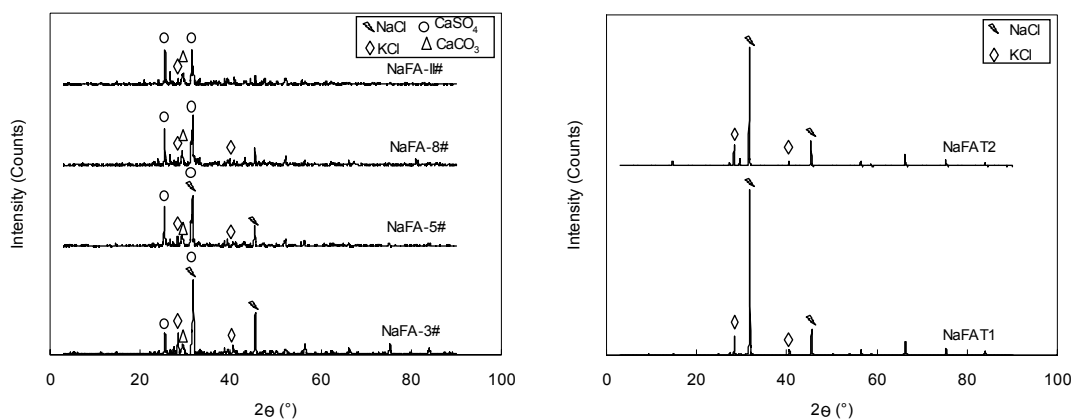
<b>Samples</b>	<b>NaCl</b>	<b>KCl</b>	<b>CaCl<sub>2</sub></b>	<b>CaCl<sub>2</sub>•2H<sub>2</sub>O</b>	<b>CaClOH</b>	<b>Friedel</b>	<b>F670</b>	<b>R</b>
<b>CaFA-0#</b>	35	11	37		4	13		0.033
<b>CaFA-3#</b>	16	6		39		24	15	0.033
<b>CaFA-6#</b>	16	3		42		32	7	0.040
<b>CaFA-8#</b>	11	3		31		36	19	0.047
<b>CaFA-II#</b>	6	2		35		33	24	0.039
<b>CaFAT1</b>	31	9		60				0.049
<b>CaFAT2</b>	31	9		60				0.045

### 3.4.3.2 LCF analysis of NaFA samples with XRD results

Similar as the analysis of CaFA, I will first check the element content of the corresponding NaFA samples. Table 3.9 lists the element concentrations in NaFA-3#, NaFA-6#, NaFA-8#, and NaFA-9#, as well as the residue mass percents. Double-washing clearly gives the minimum chlorine content and residue weight percent. The chlorine content in NaFAT1 and NaFAT2 is 9.52% and 1.81%, respectively. Figure 3.13 shows the XRD spectra of NaFAT1 and NaFAT2 residues. The XRD spectra confirm that NaCl and KCl exist in all the samples and contribute to the “A” group chlorides. Because CaClOH was not found even in the residues from the CaFA washing experiments, I exclude CaClOH here. As a result,  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ , Friedel’s salt, and F670 are the “B” group chlorides.

Table 3.9 Element concentration and residue weight percentage of NaFA-3#, NaFA-6#, NaFA-8#, and NaFA-II# (weight %)

Samples	Cl	Ca	Na	K	Al	S	Si	Residue mass percent
NaFA-3#	13.8	14.6	2.91	1.91	2.25	1.51	3.92	47.7
NaFA-6#	7.71	16.2	2.16	1.65	2.49	1.59	4.28	45.4
NaFA-8#	4.48	16.7	1.43	1.19	2.46	1.38	4.29	41.8
NaFA-II#	3.98	15.1	1.28	0.963	2.55	1.22	4.52	37.1



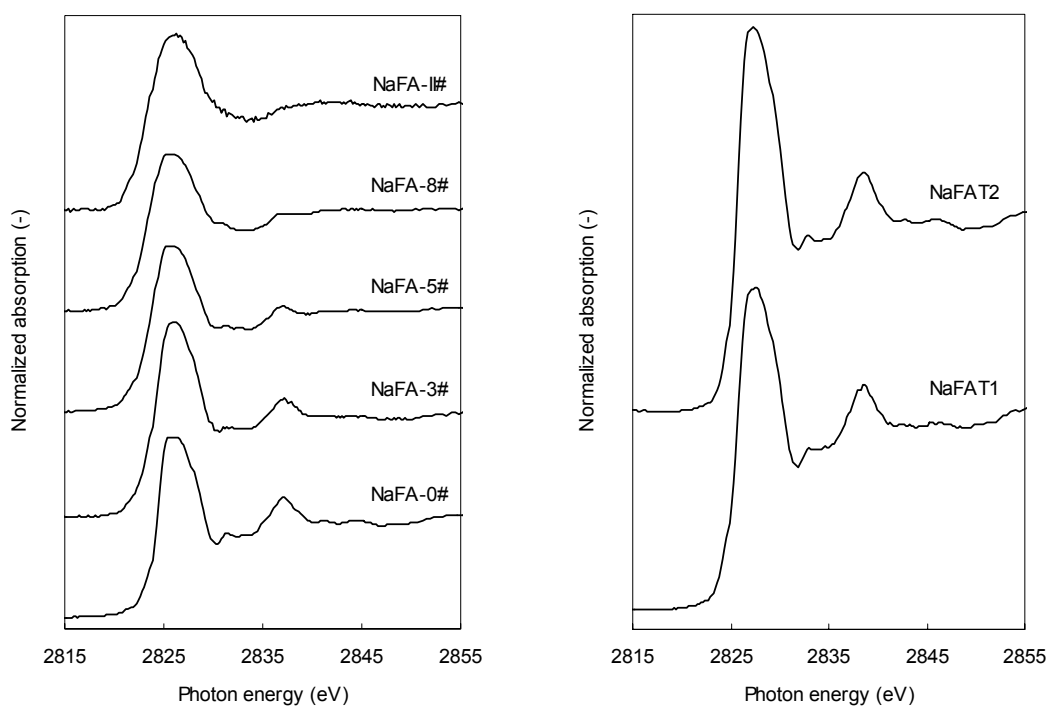
a) XRD spectra of residues

b) XRD spectra of NaFAT1 and NaFAT2

Figure 3.13 XRD spectra of NaFA-3#, 5#, 8#, and II# and NaFAT1 and NaFAT2

Figure 3.14 presents the chlorine K-edge XANES spectra of NaFA-3#, NaFA-5#, NaFA-8#, NaFA-II#, NaFAT1, and NaFAT2. The variation in spectra from NaFA-0# to

NaFA-II# is larger than that from CaFA-0# to CaFA-II#, and typical peaks corresponding to the spectrum of NaCl gradually weakened and finally disappeared in the spectrum of NaFA-II#. This pattern can be explained by the concentration of NaCl in the residues decreasing with increasing L/S ratio and washing frequency. The spectra of NaFAT1 and NaFAT2 suggest that NaCl was washed out in both the first and second steps of double-washing.



a) XANES spectra of residues

b) XANES spectra of NaFAT1 and NaFAT2

Figure 3.14 Chlorine K-edge XANES spectra of NaFA washing samples

The LCF analysis results for NaFA samples are presented in Table 3.10. In a previous study or section, I found the portion of  $\text{CaCl}_2$  is considerable in raw fly ash (RFA) <sup>20</sup>. Considering the relationship between RFA and NaFA, it is understandable that  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  is detected in the LCF results for NaFA-8#, NaFA-II#, NaFAT1, and NaFAT2. The portion of chlorine as NaCl or as KCl also decreases from NaFA-0# to NaFA-II#, the same trend as observed for CaFA. The portion of chlorine in the form of insoluble chlorides, including Friedel's salt and F670, increases. These results are discussed in detail in the following section.

Table 3.10 LCF analysis of NaFA-3#, NaFA-5#, NaFA-8#, NaFA-II#, NaFAT1, and NaFAT2  
(molar %)

Samples	NaCl	KCl	CaCl <sub>2</sub> •2H <sub>2</sub> O	Friedel	F670	R
NaFA-0#	79	12		9		0.028
NaFA-3#	47	10		38	5	0.049
NaFA-5#	53	12		35		0.058
NaFA-8#	41	13	2	44		0.068
NaFA- II #	13	6	10	71		0.072
NaFAT1	81	17	2			0.098
NaFAT2	74	7	19			0.086

### 3.4.3.3 Comparison of chloride behavior in CaFA and NaFA washing experiments

Based on the LCF analysis of washing residues and the corresponding chlorine content and residue weight percentage, the amount of chlorine in various chemical forms remaining in the residue, if 100 g CaFA or NaFA were washed under each washing condition, can be calculated, as shown in the example in Formula (3.9).

$$Cl_{NaCl} = 100g \times residue\% \times Cl\% \times m_{Cl,NaCl} \quad (3.9)$$

where  $Cl_{NaCl}$  is the amount of chlorine in the form of NaCl remaining in the residues after 100 g raw fly ash were washed;  $residue\%$  is the percentage of residue remaining after washing the fly ash; and  $m_{Cl,NaCl}$  is the molar percentage of chlorine in the form of NaCl among all chlorides in the residue. These data are from the washing experiments<sup>8</sup>. Other chlorides, such as CaClOH, KCl and so on, can be calculated in the same way as NaCl. As a result, the behavior of chlorine in different chemical form in 100 g CaFA or NaFA during washing experiments can be deduced as in Figure 3.15, which shows the decreasing trend of chlorine in each kind of chemical form in the CaFA and NaFA washing experiments. The amounts of all forms, especially those of soluble chlorides, decrease with higher L/S ratio and washing frequency. The amount of chlorine in the form of insoluble chlorides in NaFA appears to decrease slightly more than that in CaFA. The relationship among samples including CaFAT1, CaFAT2, NaFAT1, and NaFAT2 is discussed further.



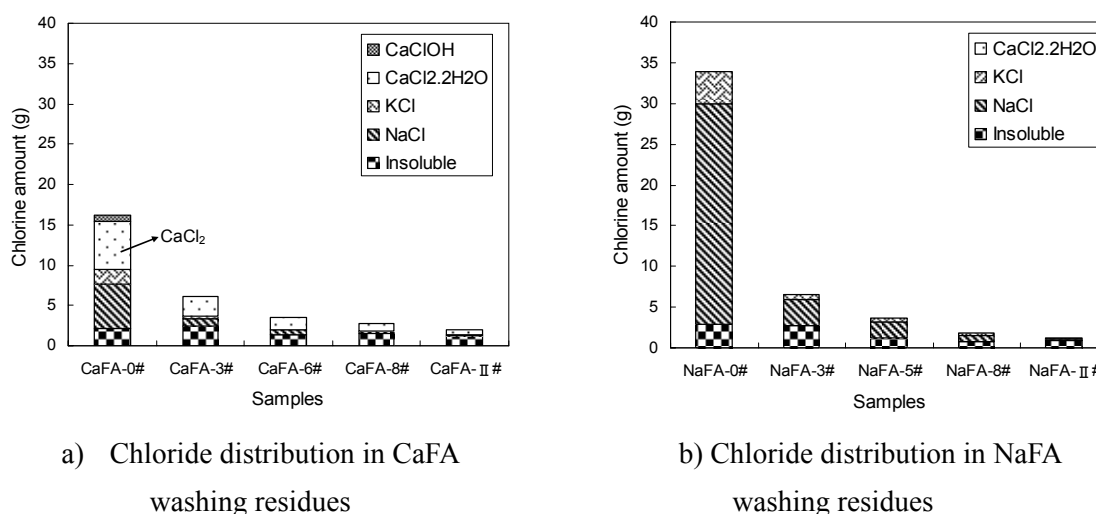


Figure 3.15 Chloride behavior in CaFA and NaFA washing experiments

With the data in Figure 3.15, I can calculate the distribution of chlorides in CaFAT1, CaFAT2, NaFAT1, and NaFAT2. For example, the chlorides in CaFAT1 represent the difference between CaFA-0# and CaFA-3# and the chlorides in CaFAT2 are the difference between CaFA-3# and CaFA-II#. I can calculate the amount of chlorine in the form of  $\text{CaCl}_2$ , NaCl, KCl, or insoluble chloride in CaFAT1, and then can determine the portion of chlorine in each form in CaFAT1. The same process can be followed for CaFAT2, NaFAT1, and NaFAT2. The corresponding results are shown in Table 3.11.

Table 3.11 Calculated chloride distribution in CaFAT1, CaFAT2, NaFAT1, and NaFAT2 (molar %)

Samples	NaCl	KCl	$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	CaClOH	Chlorine from insoluble chlorides
<b>CaFAT1</b>	44	14	35	7	
<b>CaFAT2</b>	21	8	42		29
<b>NaFAT1</b>	87	12			1
<b>NaFAT2</b>	55	10			35

Comparison of the data in Table 3.11 with the corresponding data in Tables 3.8 and 3.10 reveals some differences. For convenience, I mark the data from the LCF analysis in Table 3.8, 3.10 as “CaFAT1-L,” “CaFAT2-L,” “NaFAT1-L,” and “NaFAT2-L,” and the data in Table 3.11 are marked as “CaFAT1-D,” “CaFAT2-D,” “NaFAT1-D,” and “NaFAT2-D.” Four comparisons are made: “CaFAT1-L with CaFAT1-D,” “CaFAT2-L with CaFAT2-D,” “NaFAT1-L with NaFAT1-D,” and “NaFAT2-L with NaFAT2-D.”

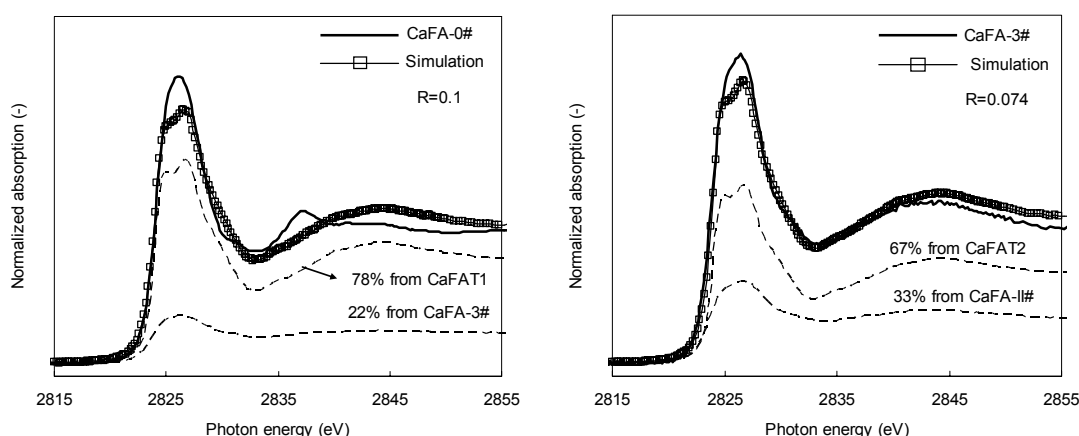
The CaFAT1-L data is not comparable to the CaFAT1-D (CaFAT2-D) data, neither is CaFAT2-L data comparable to CaFAT2-D data. However, if I include the portion of insoluble chloride in CaFAT2-D in the portion of  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ , the data for CaFAT2-L are relatively comparable to the CaFAT2-D data. In the second step of washing, it appears that some  $\text{CaCl}_2$ , originating from the insoluble chlorides in CaFA, dissolved into water. The relationship between CaFAT1-L and CaFAT1-D is somewhat more complicated. The ratio of chlorine in NaCl to the chlorine in KCl in CaFAT1-L is 3.44, which is comparable to the ratio for CaFAT1-D (3.14), while the ratio of chlorine in  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  form to that in KCl form in CaFAT1-L was 6.67, almost 2.7 times the corresponding ratio based on the CaFAT1-D data (2.5). Extra  $\text{CaCl}_2$  seems to be present. The insoluble chlorides in CaFA may have contributed to this. Friedel's salt,  $[\text{Ca}_2\text{Al}(\text{OH})_6]\text{Cl} \cdot 2\text{H}_2\text{O}$ , which I successfully used in an earlier study and section to represent the insoluble chlorides in CaFA for LCF analysis<sup>20</sup>, is the product of the system  $\text{CaO}/\text{Ca}(\text{OH})_2 - \text{Al}_2\text{O}_3/\text{Al}(\text{OH})_3 - \text{CaCl}_2/\text{CaCl}_2 \cdot 2\text{H}_2\text{O}/\text{CaCl}_2 \cdot 4\text{H}_2\text{O}/\text{CaCl}_2 \cdot 6\text{H}_2\text{O} - \text{H}_2\text{O}$ <sup>15</sup>. That system is easily built in the CaFA washing process, since there is abundant  $\text{Ca}(\text{OH})_2$ , considerable  $\text{CaCl}_2$ , and  $\text{Al}_2\text{O}_3$  in CaFA. Also, that system is reactive and will change according to the compounds and their corresponding concentrations<sup>1</sup>. Considering the complex components in CaFA, that system could likely be influenced during the washing process. If it is considered that the portion of chlorine from insoluble chlorides as chlorine in  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  form, the portion of chlorine in  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  for CaFAT2-D will change to 72%, which differs from that for CaFAT2-L by 11%. However, this result is relatively acceptable because the LCF analysis error of XANES can be about 10%. Based on the discussion above, I conclude that the insoluble chlorides in CaFA must have some reaction with  $\text{CaCl}_2$ , such as combination or release.

The relationship is not so strong for NaCl. The NaFAT1-L data are comparable to those for NaFAT1-D, while NaFAT2-L data are not comparable to the NaFAT2-D data. In the NaFAT2-L data, there is a larger portion of chlorine present in NaCl and  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  form. Compared with the data for NaFAT2-D, the extra portion of chlorine in NaCl form (19%) is the same as the portion of chlorine in  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  form in NaFAT2-L. The total amount is 38%, which is similar to the portion of chlorine present as insoluble chlorides in NaFAT2-D. If I assume that the chlorine from insoluble chlorides is in the form of NaCl and  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ , and that the distribution is equal, the phenomenon can be explained; however, it is unlikely that the distribution is equal. The fact that the data for NaFAT1-L are comparable to the NaFAT1-D data suggests that the insoluble chlorides were not affected much by the washing process in the first

step of double-washing. In other words, the injected  $\text{NaHCO}_3$  and its resulting compounds including  $\text{NaCl}$  have little relationship with the insoluble chlorides system during the washing process. As a result, I consider most of the chlorine from insoluble chlorides in NaFAT2 as chlorine in  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  form. Thus, even if 100% of the chlorine from insoluble chlorides is in  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  form, the difference between the portion of chlorine in  $\text{NaCl}$  form in NaFAT2-L and that in NaFAT2-D is 19%, and the difference between the portion of chlorine in  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  form in NaFAT2-L and that in NaFAT2-D is 16%. The degree of error in LCF analysis of XANES might be acceptable. These comparisons suggest that the insoluble chlorides in both CaFA and NaFA must be related to  $\text{CaCl}_2$ , and possibly have little relationship with  $\text{NaCl}$ ; they can combine to form  $\text{CaCl}_2$  and will release chlorides under some conditions, but little  $\text{NaCl}$  is involved.

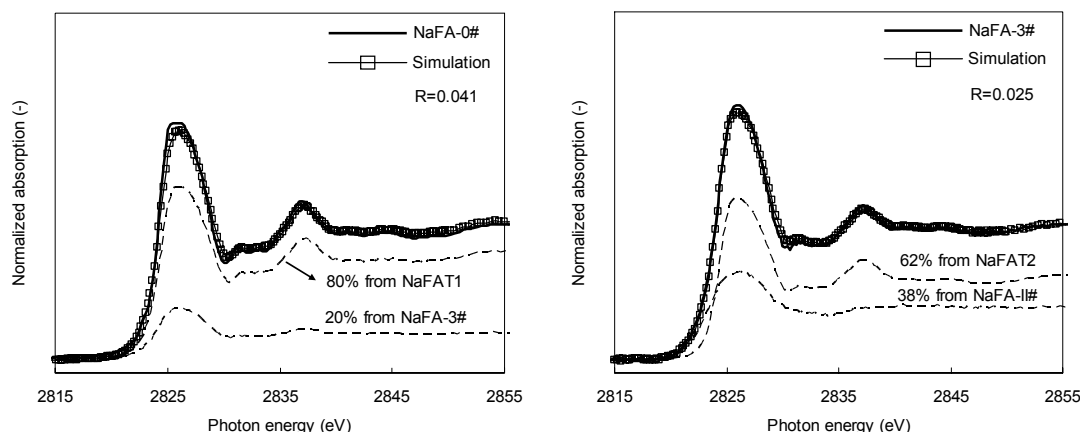
#### 3.4.3.4 Insoluble chlorides behavior in CaFA and NaFA during the washing process

The above discussion suggests that the insoluble chlorides in both CaFA and NaFA might change during the washing process. To test this hypothesis, I use the chlorine K-edge XANES spectra of CaFA-3# and CaFAT1 to simulate that of CaFA-0#, and the chlorine K-edge XANES spectra of CaFA-II# and CaFAT2 to simulate that of CaFA-3#. The same process is applied on NaFA-0# and NaFA-3#. The simulation results can be seen in Figure 3.16. The simulation for CaFA-0# and CaFA-3# is unsatisfactory, while the simulation for NaFA-0# and NaFA-3# is acceptable.



a) Simulation result of CaFA-0#

b) Simulation results of CaFA-3#



c) Simulation result of NaFA-0#

d) Simulation results of NaFA-3#

Figure 3.16 Simulation results of CaFA-0#, CaFA-3#, NaFA-0#, and NaFA-3#

From Figure 3.15, I can calculate how much chlorine went to CaFAT1, CaFAT2, NaFAT1, and NaFAT2. I can then determine the chlorine distribution between CaFA-3# and CaFAT1, CaFA-II# and CaFAT2, NaFA-3# and NaFAT1, and NaFAT-II# and NaFAT2. Relative to CaFA-0#, 35% of chlorine was left in CaFA-3# and the rest went to CaFAT1; relative to CaFA-3#, 34% of chlorine was left in CaFA-II# and 66% went to CaFAT2; relative to NaFA-0#, 18% of chlorine remained in NaFA-3# and 82% was transferred to NaFAT1; relative to NaFA-3#, 21% was kept in NaFA-II# and 78% transferred to NaFAT2. CaFA differs greatly between the data in Figure 3.16 and the above calculations.

For CaFA-0#, not only is the ratio not comparable, but also the simulation is unsatisfactory. For CaFA-3#, although the ratio is somewhat acceptable, the low R value in the simulation is not a good indicator. These results suggest that the insoluble chlorides in CaFA changed in both steps of double-washing, and the change in the first step may be stronger than that in the second step. According to the above analysis, I assume that the change in the second step of double-washing may be to release  $\text{CaCl}_2$  into water. Regarding the change in the first step of double-washing, I think it is complicated, and, as discussed in the previous section, it may involve reactions among the insoluble chlorides,  $\text{CaCl}_2$ , and some other compounds in CaFA.

For NaFA, the simulations are acceptable, and a linear relationship among NaFA-0#, NaFA-3#, and NaFAT1 can be achieved, although the relationship among NaFA-3#, NaFA-II#, and NaFAT2 is not very strong. These results suggest that the insoluble chlorides in NaFA did not change much in the first step of double-washing, which agrees with the analysis in the previous section. In the second step, the insoluble

chlorides in NaFA-3# changed, in accordance with the variation trend in the amount of insoluble chlorides shown in Figure 3.15b. The change in insoluble chlorides in the second step of double-washing may be to release  $\text{CaCl}_2$  and possibly together with a small amount of  $\text{NaCl}$ . Thus even with such high production of  $\text{NaCl}$  during the neutralization process of discharged gas, the formed insoluble chlorides in NaFA were not greatly affected by the  $\text{NaCl}$  form.

These discussions suggest that insoluble chlorides in both CaFA and NaFA have a strong relationship with  $\text{CaCl}_2$  and little with  $\text{NaCl}$ , and under some conditions they will release  $\text{CaCl}_2$ . With the data in Figure 3.15, I find that under the same conditions, the total amount of chlorine remaining in CaFA residue is larger than that left in NaFA residue; furthermore, the amount of insoluble chlorides in CaFA residue is always larger than that in NaFA residue. For example, the amount of insoluble chlorides in CaFA-II# is 31% more than that in NaFA-II#. Much more  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  remains in CaFA-II# than in NaFA-II#. Given the same conditions, the amount of chlorine removed from NaFA is much greater than that from CaFA. Thus, not only is the neutralization ability of  $\text{NaHCO}_3$  better than that of  $\text{Ca}(\text{OH})_2$ <sup>1</sup>, but the efficiency at reducing the resulting chlorides is also better in NaFA than in CaFA.

#### **3.4.4 Brief summary**

Based on the above results and discussion, I conclude that the insoluble chlorides in both CaFA and NaFA are strongly connected with  $\text{CaCl}_2$ , and have little relationship with  $\text{NaCl}$ , and will be released under some conditions. By comparing the chloride behavior in CaFA washing experiments to that in NaFA washing experiments, CaFA is found to be more dangerous as a raw material in the cement industry because more total chlorine, insoluble chlorine, and  $\text{CaCl}_2$  are retained in CaFA. The efficiency of chlorine reduction is much larger in NaFA than in CaFA. Therefore, I conclude that  $\text{NaHCO}_3$  is superior to  $\text{Ca}(\text{OH})_2$  as a neutralization reagent for reducing acid compounds in gas discharged from MSWIs.

### **3.5 Chloride behavior in washing experiments of RFA**

#### **3.5.1 Research content**

After I discussed the difference between the chlorides behavior in washing experiments of CaFA and NaFA, I will discuss the chloride behavior in washing experiments of RFA with nearly the same method. Moreover, in this part I will utilize the results of washing experiments more and strengthened it in the discussion of the LCF results.

### 3.5.2 Additional samples and method

#### 3.5.2.1 Additional samples

Single- and double-washing experiments were performed. Samples from washing experiments are listed in Table 3.12. The reason why I chose those samples is similar as the reasons explained in section 3.4.2.1. In the preliminary single-washing experiments, I found that the L/S ratio is more important to reduce chlorine content in the residue than mixing time and speed. Therefore, I fixed the mixing time and speed and set the L/S ratio from 2 to 10 in single-washing experiments. I found that when the L/S ratio was greater than 3, the chlorine content in the residue decreased much slower; hence I chose the residue from the RFA-3# experiment for analysis. Residues from the RFA-6# and RFA-8# experiments were chosen for chloride analysis from samples with  $L/S > 3$ . To determine how washing frequency affects the washing process, I selected one residue from the double-washing experiment. The washing solution is ion exchange water. The samples were dried by heating to 105°C for 24 h. The washing solution from both steps of the double-washing protocol was dried to attain solid samples RFAT1 and RFAT2. RFAT1 is the dried solid of the washing solution from the first step and is similar to the washing solution of the RFA-3# experiment. RFAT2 is the dried solid of the washing solution from the second step. This detailed process is shown in Fig. 3.17. The original RFA is marked as RFA-0#.

Table 3.12 samples from washing experiments

Code	Washing experiment	L/S ratio	Mixing time	Mixing speed
3#		3	5 min	150 rpm
6#	Single-washing	6	5 min	150 rpm
8#		10	5 min	150 rpm
II#	Double-washing	1 <sup>st</sup> step	3	5 min
		2 <sup>nd</sup> step	3	10 min

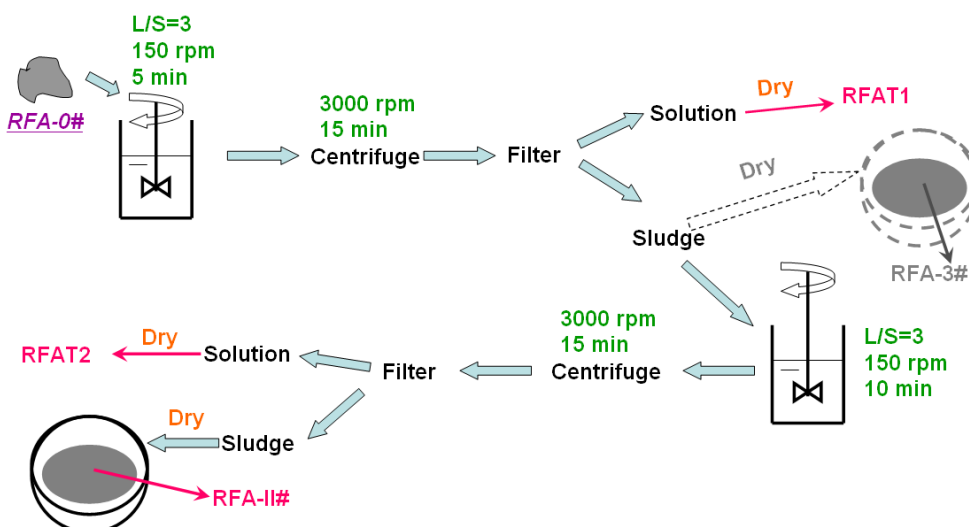


Figure 3.17 Washing process of RFA double-washing experiment

### 3.5.2.2 Analysis procedure

The analysis procedure is just like the procedure I adopted in section 3.4.2.2. I chose reference chlorides based upon elemental concentration, our previous studies<sup>20</sup>, and information found in other reports. Based on the XRD spectra of samples and their relationships among the samples, I confirmed the existence of some chlorides in the residues (“A” group chlorides); the chlorides that were left formed the “B” group chlorides. I then fixed the “A” group chlorides and added one to three more chlorides from the “B” group for LCF analysis. The combination with the minimum R value was chosen. In previous studies<sup>20</sup>, I successfully deduced the chloride chemical forms in three kinds of fly ashes by combining data from XANES with XRD data; however, in this study, the maximum number of “B” group chlorides was three.

### 3.5.2.3 XANES spectra of the reference chlorides

In the previous research and section I have deduced that about 15% of the chlorine in RFA was estimated to be in the form of NaCl, 10% in KCl, 51% in CaCl<sub>2</sub>, and the remainder was in the form of Friedel’s salt<sup>20</sup>. So the following reference chlorides will be selected in this search: NaCl, KCl, CaCl<sub>2</sub>·2H<sub>2</sub>O, [Ca<sub>2</sub>Al(OH)<sub>6</sub>]Cl·2H<sub>2</sub>O, 11CaO·7Al<sub>2</sub>O<sub>3</sub>·CaCl<sub>2</sub>. Because of the same reason I explained in the section 3.4.2.3, here I use CaCl<sub>2</sub>·2H<sub>2</sub>O instead of CaCl<sub>2</sub>, and [Ca<sub>2</sub>Al(OH)<sub>6</sub>]Cl·2H<sub>2</sub>O and its related compound 11CaO·7Al<sub>2</sub>O<sub>3</sub>·CaCl<sub>2</sub> are also included. Similarly, [Ca<sub>2</sub>Al(OH)<sub>6</sub>]Cl·2H<sub>2</sub>O is

also named as Friedel's salt, and  $11\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \cdot \text{CaCl}_2$  is named as "F670". Figure 3.18 shows the Cl K-edge XANES spectra of the reference chlorides.

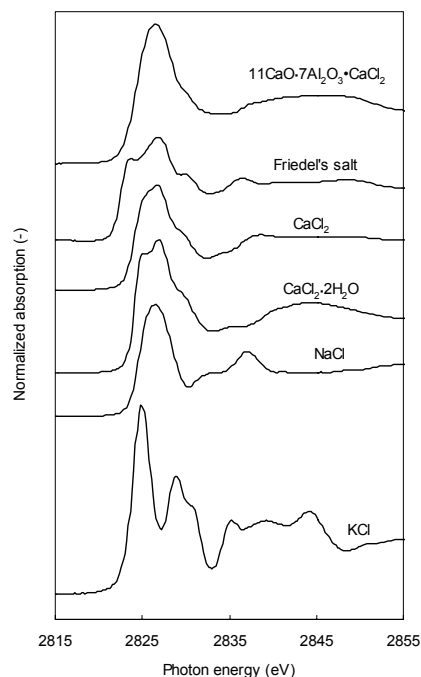


Figure 3.18 Chlorine K-edge XANES spectra of reference chlorides

Friedel's salt, calcium chloroaluminate, and calcium hydroxychloride were made and checked by XRD<sup>15, 16, 20</sup>, and other reference chlorides were purchased from Nacalai Tesque (Kyoto, Japan), Soegawa Rikagaku (Tokyo, Japan), or Nichika Corp (Kyoto, Japan).

### 3.5.3 Results and discussion

#### 3.5.3.1 Element concentration in residues from RFA washing experiments as well as residue mass percent

The concentration of Cl, Ca, Na, K, Al, S, and Si and their corresponding mass percentages are shown in Table 3.13. Chlorine content was assessed by ion chromatography (DX-AQ AI-450; Nippon Dionex KK); other elements were examined by X-ray fluorescence (XRF-1700; Shimadzu Corp.). The residue weight percent represents the ratio of the amount of remaining dried washed residue to the amount of RFA that was used in the washing experiments. Data shown in Table 3.13 suggest that



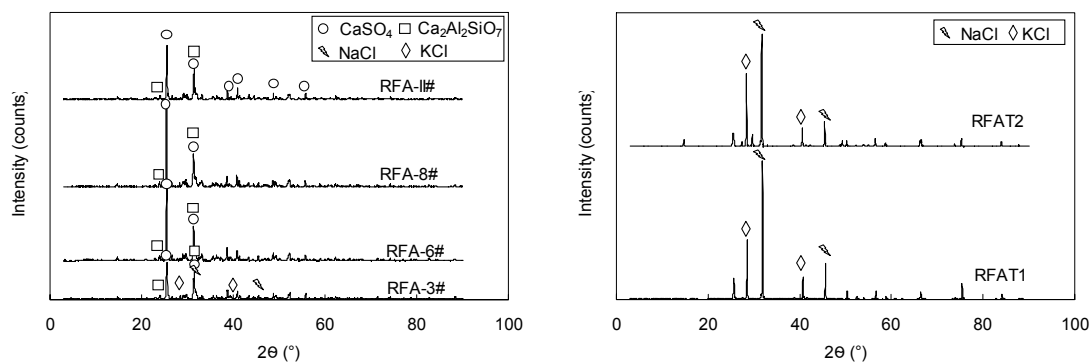
double-washing does significantly change the chlorine content or the residue mass percent. The L/S ratio has less of an influence than washing frequency on the chlorine content and mass residue when the L/S ratio is larger than 6, because in the RFA-6# experiment, I used the same amount of water as in the double-washing protocol, and in the RFA-8# experiment, I used more water during double-washing. The chlorine concentrations in RFAT1 and RFAT2 are 1.66% and 0.511%, respectively.

Table 3.13 Concentration of some elements in the RFA washing residues and residue weight percent (weight %)

<b>Samples</b>	<b>Cl</b>	<b>Ca</b>	<b>Na</b>	<b>K</b>	<b>Al</b>	<b>S</b>	<b>Si</b>	<b>Residue weight percent</b>
<b>RFA-3#</b>	2.81	23.0	0.773	1.14	3.50	3.76	5.31	89.2
<b>RFA-6#</b>	2.11	24.5	0.831	1.29	3.39	3.88	5.22	87.0
<b>RFA-8#</b>	1.76	24.2	0.807	1.23	3.49	3.94	5.38	86.1
<b>RFA-II#</b>	0.961	24.5	0.682	1.02	3.71	3.86	5.62	84.8

### 3.5.3.2 XRD and LCF analysis of samples

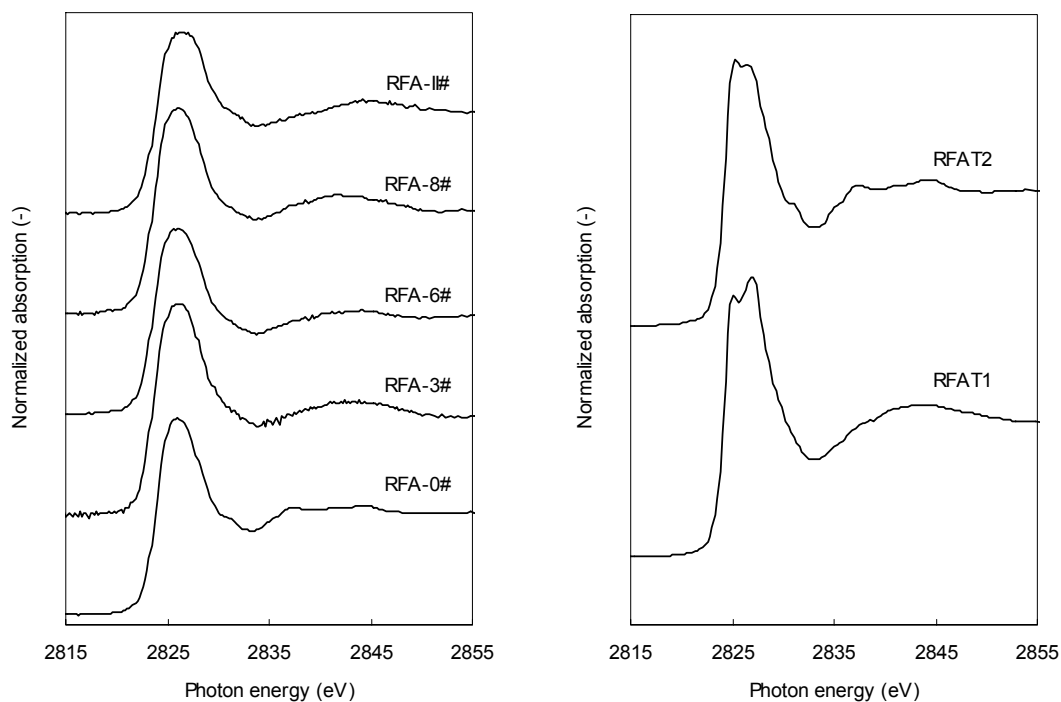
RFA-3#, RFA-6#, RFA-8#, RFA-II#, RFAT1, and RFAT2 were examined by XRD (Fig. 3.19), and RFA-3# is confirmed to contain NaCl and KCl. Because RFA-6# and RFA-8# comprise residues from single-washing, the presence of NaCl and KCl in RFAT1 suggests that NaCl and KCl must also exist in RFA-6# and RFA-8#. Because RFAT2 is the dried solid of the washing solution from the second step of the double-washing experiment, NaCl and KCl should also be found in RFA-II#; however, the concentration of these chloride salts might be too low to be detected by XRD. NaCl and KCl, therefore, are designated as “A” group chlorides for RFA-3#, RFA-6#, RFA-8#, and RFA-II#. The remaining chlorides are  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ , Friedel’s salt, and F670.



a) XRD spectra of residues

b) XRD spectra of RFAT1 and RFAT2

Figure 3.19 XRD results of samples from RFA washing experiments



a) XANES spectra of residues

b) XANES spectra of RFAT1 and RFAT2

Figure 3.20 Chlorine K-edge XANES spectra of RFA washing samples

Figure 3.20 shows the chlorine K-edge XANES spectra of RFA-0#, RFA-3#, RFA-6#, RFA-8#, RFA-II#, RFAT1, and RFAT2. The shapes of the spectra from the residues are similar, with a vale appearing after the first peak. The absorption threshold is ~2,820 eV, and the photon energy of the atomic absorption peak is ~2,826 eV. The spectrum of RFA-0# has more fine structures compared to RFA-3#, RFA-6#, RFA-8#, and RFA-II#,

and the differences between these individual samples are related to the height of the atomic absorption jump and the overall curve characteristics. The spectrum of RFAT1 has many characteristics that are similar to the spectrum of  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ , which suggests that  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  might also exist in residues from single-washing experiments. Although the spectrum of RFAT2 has some NaCl characteristics (e.g., a peak  $\sim 2,837$  eV), the shape of the spectrum of RFAT2 is most like that of  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ , suggesting that a portion of chlorine in RFAT2 was in the NaCl form.

I next analyze the chlorine K-edge XANES spectrum of RFA-3# and conclude that the “A” group chlorides in RFA-3# are NaCl and KCl and that the “B” group chlorides are  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ , Friedel’s salt, and F670. Hence, I fix NaCl and KCl and combine one more compound from the “B” group for LCF analysis. The results are shown in Table 3.14. Among mixtures [1] to [4], mixture [4] has the minimum R value, which suggests that F670 is possibly in RFA-3# among the “B” group chlorides. Next, I fix NaCl, KCl, and F670 and add one more chloride to get combination [5]. I then try the combination of “NaCl + KCl +  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  + Friedel’s salt + F670” and the result is combination [6] (Table 3.14). Mixture [6] has the lowest R value of all the mixtures. The portion of chlorine in the insoluble chloride form in combination [4], combination [5], and combination [6] are 72%, 79%, and 44%, respectively. The remaining chlorine in RFA-8# is  $\sim 61\%$  of the chlorine in RFA-3#, which suggests that the portion of chlorine in an insoluble chloride form in RFA-3# should be less than 61%. Therefore, combination [6] is the most reliable. Using similar analyses, the distributions of chloride in RFA-6#, RFA-8#, and RFA-II# are also obtained (Table 3.15). For comparison, I include the distribution of chlorides in RFA-0#.

Table 3.14 LCF analysis results of RFA-3# (molar %)

Code	NaCl	KCl	$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	Friedel	F670	R
[1]	58	42				0.143
[2]	23	21	56			0.091
[3]	29	19		52		0.083
[4]	5	23			72	0.076
[5]	6	15		33	46	0.049
[6]	12	11	33	38	6	0.043

Table 3.15 LCF analysis results of RFA-0#, RFA-3#, RFA-6#, RFA-8#, RFA- II #, RFAT1 and RFAT2 (molar %)

Samples	NaCl	KCl	CaCl <sub>2</sub>	CaCl <sub>2</sub> ·2H <sub>2</sub> O	Friedel	F670	R
<b>RFA-0#</b>	15	10	51		25		0.046
<b>RFA-3#</b>	12	11		33	38	6	0.043
<b>RFA-6#</b>	13	9		32	45	1	0.052
<b>RFA-8#</b>	11	11		20	42	16	0.052
<b>RFA- II #</b>	6	3		19	40	33	0.078
<b>RFAT1</b>	25	6		69			0.057
<b>RFAT2</b>	30	10		60			0.069

Because RFA (RFA-0#) is gathered from the boiler of the incinerator, and after I got the sample I sealed it in a bottle, I use CaCl<sub>2</sub> in the combination for RFA-0#. Friedel's salt and F670 are regarded as insoluble chlorides. From the data in Table 3.15, it can be found that the portion of insoluble chlorides gradually goes higher with the increasing of L/S ratio or washing frequency, while, the portion of soluble chlorides such as NaCl, KCl and CaCl<sub>2</sub>·2H<sub>2</sub>O decreases.

With the increasing value of R from RFA-0# to RFA-II#, it might suggest the insoluble chlorides have changed during the washing process. I will discuss it later.

### 3.5.3.3 Chloride behavior in RFA washing experiments

Using results from LCF analysis of the residues shown in Table 3.15 and the chlorine content and residue weight percent from Table 3.13, the amount of chlorine in different chemical forms in the RFA and the washed residues can be calculated by Formula 3.9 after 100 g of RFA was washed under each condition.

Figure 3.21 shows the amount of chlorine in different chemical forms in the residues. Both the soluble and insoluble portions decrease, especially in residues from RFA-6#, RFA-8#, and RFA-II#. I include Friedel's salt and F670 together as "insoluble chloride"; Friedel's salt belongs to the AFm phases in the cement field<sup>1</sup>. These phases include Kuzel's salt (3CaO·Al<sub>2</sub>O<sub>3</sub>·0.5CaCl<sub>2</sub>·0.5CaSO<sub>4</sub>·10H<sub>2</sub>O), sulfate AFm (3CaO·Al<sub>2</sub>O<sub>3</sub>·CaSO<sub>4</sub>·nH<sub>2</sub>O), hydroxy AFm (3CaO·Al<sub>2</sub>O<sub>3</sub>·Ca(OH)<sub>2</sub>·nH<sub>2</sub>O), hemicarboaluminate (3CaO·Al<sub>2</sub>O<sub>3</sub>·0.5Ca(OH)<sub>2</sub>·0.5CaCO<sub>3</sub>·10.5H<sub>2</sub>O), monocarboaluminate (3CaO·Al<sub>2</sub>O<sub>3</sub>·CaCO<sub>3</sub>·10H<sub>2</sub>O), stratlingite (2CaO·Al<sub>2</sub>O<sub>3</sub>·SiO<sub>2</sub>·8H<sub>2</sub>O), and U-phase (4CaO·0.9Al<sub>2</sub>O<sub>3</sub>·1.1SiO<sub>2</sub>·0.5Na<sub>2</sub>O·16H<sub>2</sub>O)<sup>1</sup>. According to Glassers, Friedel's salt can easily change to Kuzel's salt or U-phase in the presence of

$\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  or  $\text{OH}^-$ . In other studies<sup>21</sup>, at least 80% of insoluble chlorine (which was confirmed to be Friedel's salt by XRD) could be removed by continuous washing 16 at pH 9 and in the presence of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$ . The pH values of all washing solutions in our experiments are less than 10. I also checked the concentration of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  in RFAT1 and RFAT2. RFAT1 contained 3,466 mg/l  $\text{Ca}^{2+}$  and 2,258 mg/l  $\text{SO}_4^{2-}$ , and RFAT2 contained 1,783 mg/l  $\text{Ca}^{2+}$  and 2,497 mg/l  $\text{SO}_4^{2-}$ . Hence, Friedel's salt could have gradually changed into Kuzel's salt or U-phase.

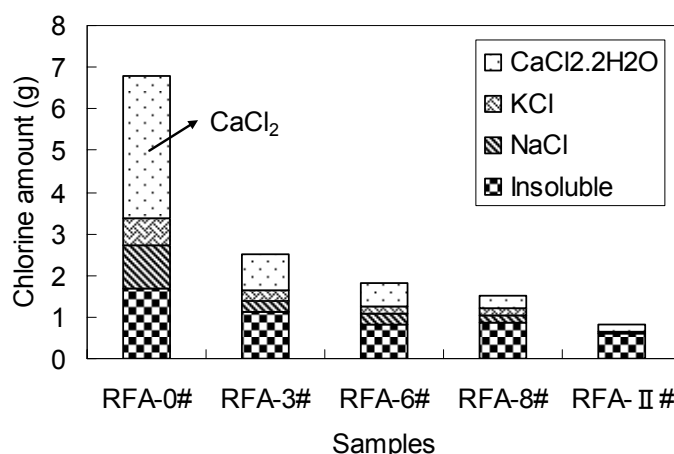


Figure 3.21 Behavior of chlorine in different chemical form in washing residues of RFA

Double-washing is generally more effect in removing soluble chlorides than single-washing (Fig. 3.21). In the RFA-6# experiment (single-washing), the same L/S ratio as in the RFA-II# experiment (double-washing) was used, but less soluble and insoluble chlorides remained in RFA-II# than in RFA-6#. Hence, some insoluble chlorides were washed out. Moreover, some chlorides in RFAT1 and RFAT2 must have come from the insoluble chlorides in RFA. This may be particularly true for chlorides in RFAT2 because reductions in the amount of chlorine from insoluble chlorides are the largest from RFA-3# to RFA-II#. Nevertheless, the above information does not reveal the kinds of chlorides released by the insoluble chlorides in RFA or their proportional amounts. Therefore, I calculated the chloride distribution in RFAT1 and RFAT2 from the data given in Fig. 3.21; the chloride distributions are shown in Table 3.16. Because the difference of chlorine amount in different chloride forms between RFA-0# and RFA-3# is the chloride distribution in RFAT1, and that difference between RFA-3# and RFA-II# is the chloride distribution in RFAT2. For example, there is 1.04 gram chlorine in NaCl form in RFA-0#, and 0.29 gram chlorine in NaCl form in RFA-3#, so there should be 0.75 gram chlorine in NaCl form which went to

RFAT1. By the same calculation method, I can calculate how much chlorine in other chloride form in RFAT1, and then I can get the molar portion of chlorine in different chloride form in RFAT1 (Refer to Table 3.16). By comparing data in Table 3.16 with data in Table 3.15, I can deduce what kinds of chlorides the chlorine released from insoluble chlorides formed, NaCl, KCl, or  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ . Using these data, I also compared the LCF data with the calculated data in Table 3.16; for RFAT2, the amount of chlorine in  $\text{CaCl}_2$  or NaCl are similar, but the level of KCl is different. Similarly, chlorine released from insoluble chlorides in RFAT1 appears to be in the form of  $\text{CaCl}_2$  and NaCl.

Table 3.16 chlorides distribution in RFAT1 and RFAT2 deduced from the former data (molar %)

Samples	NaCl	KCl	$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	Chlorine from insoluble chlorides
RFAT1	17	9	61	13
RFAT2	14	15	40	31

Next, the concentration of  $\text{Na}^+$  and  $\text{K}^+$  in RFAT1 and RFAT2 was assessed. The molar amount of each element was calculated based on the concentration of each element per liter. The molar ratios of  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Ca}^{2+}$  were calculated and are shown in Table 3.17. The  $\text{Ca}^{2+}$  increases in the second step of double-washing, and  $\text{Na}^+$  and  $\text{K}^+$  decrease in this step. Since soluble calcium compounds are relatively rare, I speculate that most of the chlorides from insoluble chlorides were in the form of  $\text{CaCl}_2$ , which is in accordance with our analyses. Taking together, I conclude that the washing process removes mostly  $\text{CaCl}_2$ .

Table 3.17 concentration and molar ratio of  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Ca}^{2+}$  in RFAT1 and RFAT2

Samples		$\text{Na}^+$	$\text{K}^+$	$\text{Ca}^{2+}$
RFAT1	Concentration (mg/l)	4141	3745	3466
	Molar ratio (%)	49.6	26.5	23.9
RFAT2	Concentration (mg/l)	1547	1368	1783
	Molar ratio (%)	45.8	23.9	30.3

#### 3.5.3.4 Insoluble chlorides behavior in RFA during washing experiments

Collectively, our results suggest that the insoluble chlorides might have changed during

the washing process. Therefore, I use the chlorine K-edge XANES spectra of RFA-3# and RFAT1 to simulate RFA-0# and the chlorine K-edge XANES spectra of RFA-II# and RFAT2 to simulate RFA-3# (Fig. 3.22). From the data shown in Fig. 3.21, I calculated the amount of chlorine move to RFAT1 and RFAT2 to determine the chlorine distribution between RFAT1 and RFA-3#, and chlorine distribution between RFAT2 and RFA-II#. Relative to RFA-0#, 34% of the chlorine went to RFA-3# and 66% of the chlorine was derived from RFAT1. Relative to RFA-3#, 35% of the chlorine remained in RFA-II# and 65% of the chlorine went to RFAT2. I express those relationships in the following formulas.

$$Cl_{RFA-3\#} = 34\% \times Cl_{RFA-0\#} \quad (3.10)$$

$$Cl_{RFAT1} = 66\% \times Cl_{RFA-0\#} \quad (3.11)$$

$$Cl_{RFA-II\#} = 35\% \times Cl_{RFA-3\#} \quad (3.12)$$

$$Cl_{RFAT2} = 65\% \times Cl_{RFA-3\#} \quad (3.13)$$

Where  $Cl_{RFA-3\#}$  is the amount of chlorine in the residue of RFA-3#;  $Cl_{RFA-0\#}$  is the amount of chlorine in RFA-0#;  $Cl_{RFAT1}$  is the amount of chlorine in the sample of RFAT1;  $Cl_{RFA-II\#}$  is the amount of chlorine in the residue of RFA-II#; and  $Cl_{RFAT2}$  is the amount of chlorine in the sample of RFAT2. According to Formula 3.10, 3.11, 3.12 and 3.13, the relationship of the absorption coefficients of chlorine in RFA-0#, RFA-3# and RFAT1 should be as Formula 3.14, and that of the absorption coefficient of chlorine in RFA-3#, RFA-II# and RFAT2 should be as Formula 3.15.

$$Deduce: \mu_{Cl,RFA-0\#} = 34\% \mu_{Cl,RFA-3\#} + 66\% \mu_{Cl,RFAT1} \quad (3.16)$$

$$\mu_{Cl,RFA-3\#} = 35\% \mu_{Cl,RFA-II\#} + 65\% \mu_{Cl,RFAT2} \quad (3.17)$$

Where  $\mu_{Cl,RFA-0\#}$  is the absorption coefficient of X-ray from 2,815 eV to 2,855 eV by chlorine in the residue of RFA-0#;  $\mu_{Cl,RFA-3\#}$  is the absorption coefficient of X-ray from 2,815 eV to 2,855 eV by chlorine in the residue of RFA-3#;  $\mu_{Cl,RFAT1}$  is the absorption coefficient of X-ray from 2,815 eV to 2,855 eV by chlorine in RFAT1;  $\mu_{Cl,RFA-II\#}$  is the absorption coefficient of X-ray from 2,815 eV to 2,855 eV by chlorine in the residue of RFA-II#; and  $\mu_{Cl,RFAT2}$  is the absorption coefficient of X-ray

from 2,815 eV to 2,855 eV by chlorine in RFAT2.

While, based on the data in Figure 3.22, actually, the relationships are as Formula 3.16 and 3.17.

$$\text{Actual} : \mu_{Cl, RFA-0\#} = 60\% \mu_{Cl, RFA-3\#} + 40\% \mu_{Cl, RFAT1} \quad (3.16)$$

$$\mu_{Cl, RFA-3\#} = 30\% \mu_{Cl, RFA-II\#} + 70\% \mu_{Cl, RFAT2} \quad (3.17)$$

By comparing Formula 3.14 with Formula 3.16 and Formula 3.15 with Formula 3.17, it can be found that the simulation of RFA-0# does not demonstrate a linear relationship among RFA-0#, RFA-3#, and RFAT1, while that of RFA-3# exhibits a linear relationship with RFA-3#, RFA-II#, and RFAT2. However, the R value of the simulation of RFA-3# with RFA-II# and RFAT2 is 0.072, and the R value of the LCF analysis of RFA-II# is 0.078 (Table 3.15), both of which are considered high. These results suggest that the insoluble chlorides changed in both the first and second steps of the double-washing procedure and that most of the released chlorides were  $\text{CaCl}_2$ . The chlorine content in RFAT1 and RFAT2 and the data from Table 3.16 are then used to calculate the amount of chlorine released from insoluble chlorides: 0.216% in RFAT1 and 0.158% in RFAT2. In all, these analyses are consistent with the former measurements that indicate a decreased amount of chlorine in insoluble chlorides with increasing L/S ratios or washing frequencies.

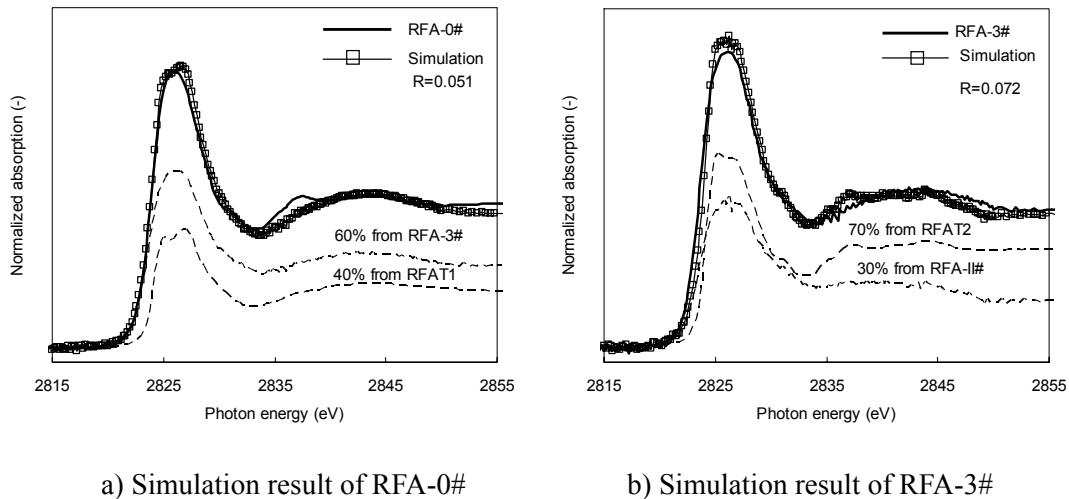


Figure 3.22 Simulation results of RFA-0# and RFA-3#



### 3.5.4 Brief summary

The analysis of XANES spectra by LCF combined with XRD is effective for the determination of chloride behavior from RFA. Our washing experiments further suggest that suitable combinations of chloride compounds in the washing residues of RFA. Furthermore, I found that it was reasonable to use Friedel's salt and its related compound as standards for the insoluble chlorides in RFA and its residues. The insoluble chlorides in RFA are complex and are strongly related to  $\text{CaCl}_2$  or similar chloride compounds. They appear to change during the washing process, and this released chloride was mostly found in the  $\text{CaCl}_2$  form. Double-washing was more effective than single-washing to reduce chlorides from FA.

Based on the discussion above, the method that LCF analysis of XANES spectra combined with XRD is effective. With the results from washing experiments, I can get the suitable combination.

## 3.6 Conclusion

I used the method of combining XANES with XRD to do the speciation analysis of chlorides in three kinds of fly ashes and their corresponding residues from washing experiments. The method is effective and useful.

I found that 15% of the chlorine in raw fly ash (RFA) was estimated to be in the form of NaCl, 10% in KCl, 50% in  $\text{CaCl}_2$ , and the remainder in the form of Friedel's salt, fly ash collected in a bag filter with the injection of calcium hydroxide for acid gas removal (CaFA) contained 35% of chlorine as NaCl, 11% as KCl, 37% as  $\text{CaCl}_2$ , 13% as Friedel's salt, and the remaining 4% as  $\text{CaClOH}$ , and in fly ash collected in a bag filter with the injection of sodium bicarbonate for acid gas removal (NaFA), approximately 79% of chlorine was in NaCl, 12% was in KCl, and 9% was in Friedel's salt.

By comparing the chloride behavior in the residues of CaFA and those in NaFA, I concluded that NaFA is more suitable for being recycled as the raw material in cement industry, because under the same condition, both the total amount of left chlorine and that of the chlorine in the form of insoluble chlorides in the residues of NaFA are less than those in CaFA as well as the amount of chlorine in  $\text{CaCl}_2$  related form, which is more dangerous to cement than NaCl and KCl. Another result is that the insoluble chlorides in both CaFA and NaFA changed during the washing process. They are

strongly related to  $\text{CaCl}_2$  and will release some  $\text{CaCl}_2$  into water phase during the washing process. Double washing is effective to remove soluble chlorides from fly ash. As to insoluble chlorides, the effect is not so obvious. The analysis of chloride behavior of residues from RFA washing experiments shows the similar trends that double washing has more significant effect than single washing on reducing the amount of residue and chlorine in RFA, and the insoluble chlorides in RFA is strongly related to  $\text{CaCl}_2$ , which will be released during the washing process.

However, there are limitations in the application of that method. First of all, there must be crystal compounds in considerable concentration among the chemical forms that need to be identified, so that I can use XRD to prove the existence of some crystal. Second, there should be sound reasons to include the amorphous compounds or crystal compounds that can not be identified by XRD in the LCF analysis. Third, because of the error of LCF analysis and the instability of the spectra of reference compounds, I had better utilize the results from some related experiments, for example, here they are the washing experiments, to examine the reliability of the LCF analysis results.

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## 4 RESEARCH OF CALCINATING PROCESS

### 4.1 Introduction

Calcinating is an important step of WCCB system after the washing process. One aspect is that calcinating is effective to stabilize and detoxify fly ash<sup>1-3</sup>, the other aspect is that most of the chlorides are of low melting points<sup>4</sup>, and that calcinating can evaporate some chlorides and so reduce the chlorine content. In this chapter, I will mainly discuss the influence of calcinating on the chlorides in the washed residue of three kinds of fly ashes. As found in Chapter 3, there are very possibly chloride hydrates such as Friedel's salt,  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  or  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  in the washed residues<sup>5,6</sup>, so heating the residues can reduce the residue mass. And Friedel's salt is sensitive to heat<sup>7</sup>, when it is heated, Friedel's salt will decompose, which benefits the third step of WCCB system—changing the treated fly ash with bottom ash together to the raw material in cement industry. Besides the chloride hydrates, there must be other hydrates or compounds unstable or of low melting point existing in the washed residue, such as  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , C,  $\text{CaCO}_3$ , which all contribute to the mass of residue.

Moreover, as I want to utilize the MSW incinerator to process the heating process and I want to get the information of sending the residue directly into the rotary kiln in cement industry, I will process the calcinating experiment from 400°C to 1,200°C. According to the previous researches<sup>8,9</sup>, I set the longest dwell time or heating time as 2 hours, and I tried two kinds of atmosphere, pure  $\text{N}_2$  and 10%  $\text{O}_2$  with 90%  $\text{N}_2$  for balance. Similar as the procedures I used in the research of washing process, first I carried out the preliminary experiment to find out the more critical factors in calcinating process, and then I designed the formal experiment condition for the residues of all the three kinds of fly ashes. Besides chlorine, I checked the variation of the concentration of  $\text{Cr}^{6+}$  in the treated residues, because  $\text{Cr}^{6+}$  is sensitive to  $\text{O}_2$  and heat with the existence of unburned carbon.

### 4.2 Experiment material and method

#### 4.2.1 Experiment material

Washed residues from 17# washing experiment (3:1, 150 rpm, 5min—3:1, 150 rpm, 10 min, refer to Table 2.7) of the three kinds of fly ashes were used: RFA-II#, CaFA-II# and NaFA-II#. The composition of the three kinds of fly ash was examined by X-ray fluorescence (XRF-1700, Shimadzu Corporation) and ion chromatography (DX-AQ AI-450, DIONEX Co., Ltd., Japan). The element composition of those residues is shown in Table 4.1.

Table 4.1 Element content of RFA-II#, CaFA-II# and NaFA-II# (weight %)

Element	RFA-II#	CaFA-II#	NaFA-II#	Element	RFA-II#	CaFA-II#	NaFA-II#
<b>O</b>	45.0	41.3	34.8	<b>K</b>	0.985	0.865	0.963
<b>Si</b>	5.42	4.23	4.52	<b>Na</b>	0.663	0.694	1.29
<b>C</b>	2.78	11.4	14.7	<b>Ti</b>	1.48	1.15	1.44
<b>Cl</b>	0.961	2.67	3.98	<b>Mg</b>	1.35	1.34	1.39
<b>S</b>	3.72	2.33	1.22	<b>P</b>	0.740	0.400	0.603
<b>Ca</b>	23.5	26.0	15.1	<b>Al</b>	3.59	2.17	2.55
<b>Fe</b>	5.27	1.97	2.33	<b>Cu</b>	0.551	0.148	0.690
<b>Zn</b>	2.11	2.63	8.13	<b>Pb</b>	0.954	0.369	6.38
<b>Br</b>	0.0164	0.0440	0.139	<b>Cr</b>	0.196	0.0605	0.104

#### 4.2.2 Experiment method

The washed residue was heated by High Temperature Tube Ovens (KRB-24HH, ISUZU SEISAKUSHO Co., Ltd; KTF-045, Kyoto Thermo System Co., Ltd.).

##### 4.2.2.1 Preliminary experiments

Based on literature review <sup>8, 9</sup>, I found there are three main important parameters to affect the final results of calcinating and they are heating temperature, dwell time and atmosphere. I first tested the importance of heating temperature and dwell time. The condition of preliminary experiments is shown in Table 4.2. The atmosphere flux is fixed as N<sub>2</sub> 25 ml/min, because if the flux is too big, the gas will bring away some of the residues, while I also need proper gas flux to move. I set the heating temperature as 700°C, 800°C and 900°C respectively, because normally the highest temperature in MSW incinerator is 900°C. In the preliminary experiments, about 5 gram residue

(RFA-II#, CaFA-II#, NaFA-II#) was used in each experiment condition and each experiment condition was repeated for at least twice.

Table 4.2 Experiment conditions for preliminary experiment

Code	Heating temperature (°C)	Dwell time (hr)	Code	Heating temperature (°C)	Dwell time (hr)
P-1#	700	0.5	P-6#	800	2
P-2#	700	1	P-7#	900	0.5
P-3#	700	2	P-8#	900	1
P-4#	800	0.5	P-9#	900	2
P-5#	800	1			

In preliminary experiments, I heated the heating tube to the target temperature with the chosen atmosphere, which I named that time range as heating time. And then I put the sample in the heating tube and kept the heating tube at the target temperature for 0.5 hour, 1 hour or 2 hours, which I call as dwell time. However, in the formal experiments, I put the sample in the heating tube at room temperature and then heated them together with set program including heating period and dwelling period. The reason why I adopted different heating method is that one is because of the slow heat transferring characteristics of the heating tube, which is not able to endure big thermal shock, and the other reason is that I want to get some information about the influence of heating method on chlorine reduction and other factors, which would be the further study of calcinating process.

In the preliminary experiments I only checked the loss of residue (LOR) expressed in Formula 4.1

$$LOR = \frac{Mass_{washed-dried} - Mass_{washed-dried-calcinated}}{Mass_{washed-dried}} \times 100\% \quad (4.1)$$

Where  $Mass_{washed-dried}$  is the weight of residue being washed and dried in each experiment and  $Mass_{washed-dried-calcinated}$  is the weight of residue after being washed, dried and calcinated.

Figure 4.1 shows the LOR value of each kind of fly ashes under preliminary experiments.

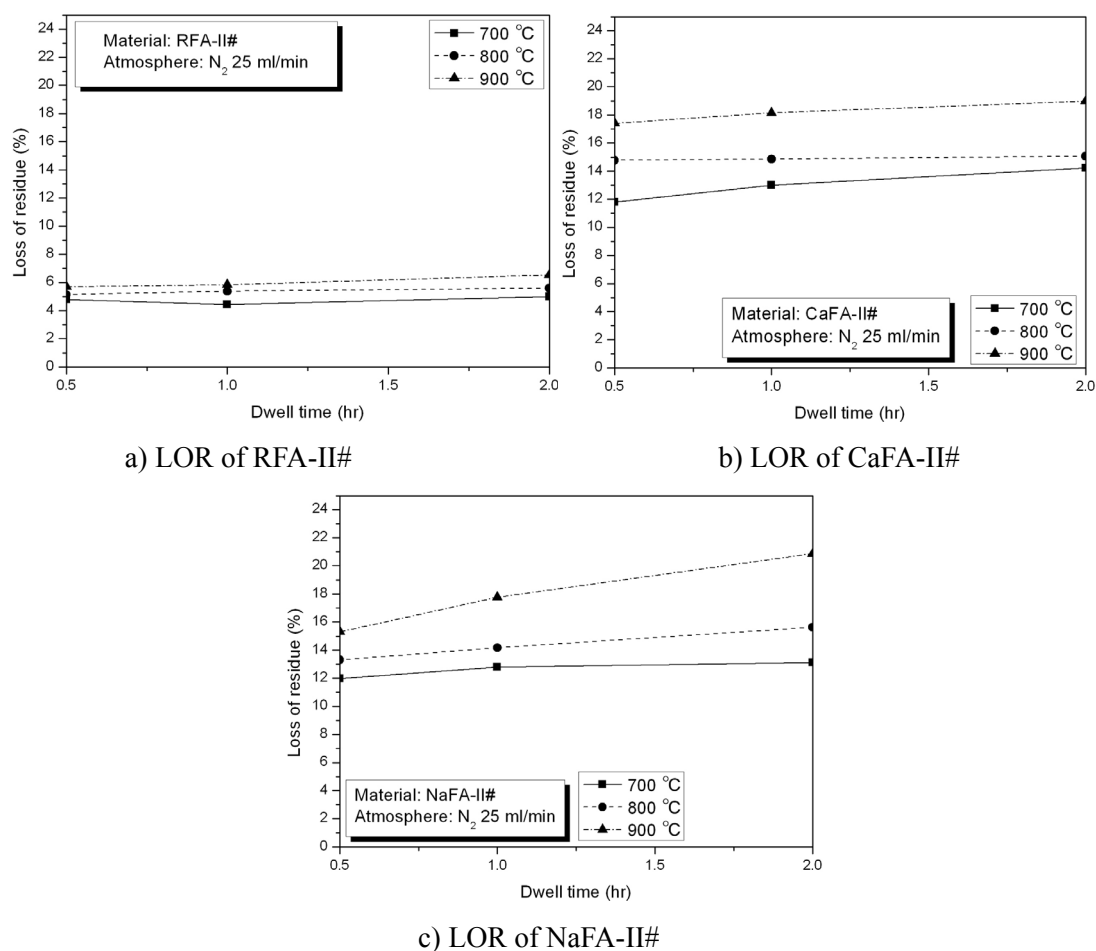


Figure 4.1 LOR results of calcinating preliminary experiments

From Figure 4.1 it can be found that the influence of heating temperature is more obvious than dwell time on the LOR value of residues. At any fixed dwell time the LOR value at 900°C is the maximum, the second biggest value is at 800°C and the minimum is at 700°C. Normally even if the residue is heated at 700°C or 800°C for 2 hours, the LOR value is less than that in 800°C or 900°C for 0.5 hour.

As I explained before that Cr<sup>6+</sup> is sensitive to O<sub>2</sub> and heating with the existence of unburned carbon, I also checked the variation of Cr<sup>6+</sup> in the preliminary experiments. Figure 4.2 shows the corresponding results. For RFA-II#, the variation of Cr<sup>6+</sup> concentration in the residues is more influenced by temperature than by dwell time, for CaFA-II# and NaFA-II# dwell time began to show its impact, especially for NaFA-II#, however, in all, the Cr<sup>6+</sup> concentration in CaFA-II# and NaFA-II# is not high, the maximum Cr<sup>6+</sup> concentration of which is 21.8 mg/ kg and 7.32 mg/ kg, respectively, while Cr<sup>6+</sup> concentration in RFA-II# is 274 mg/ kg.

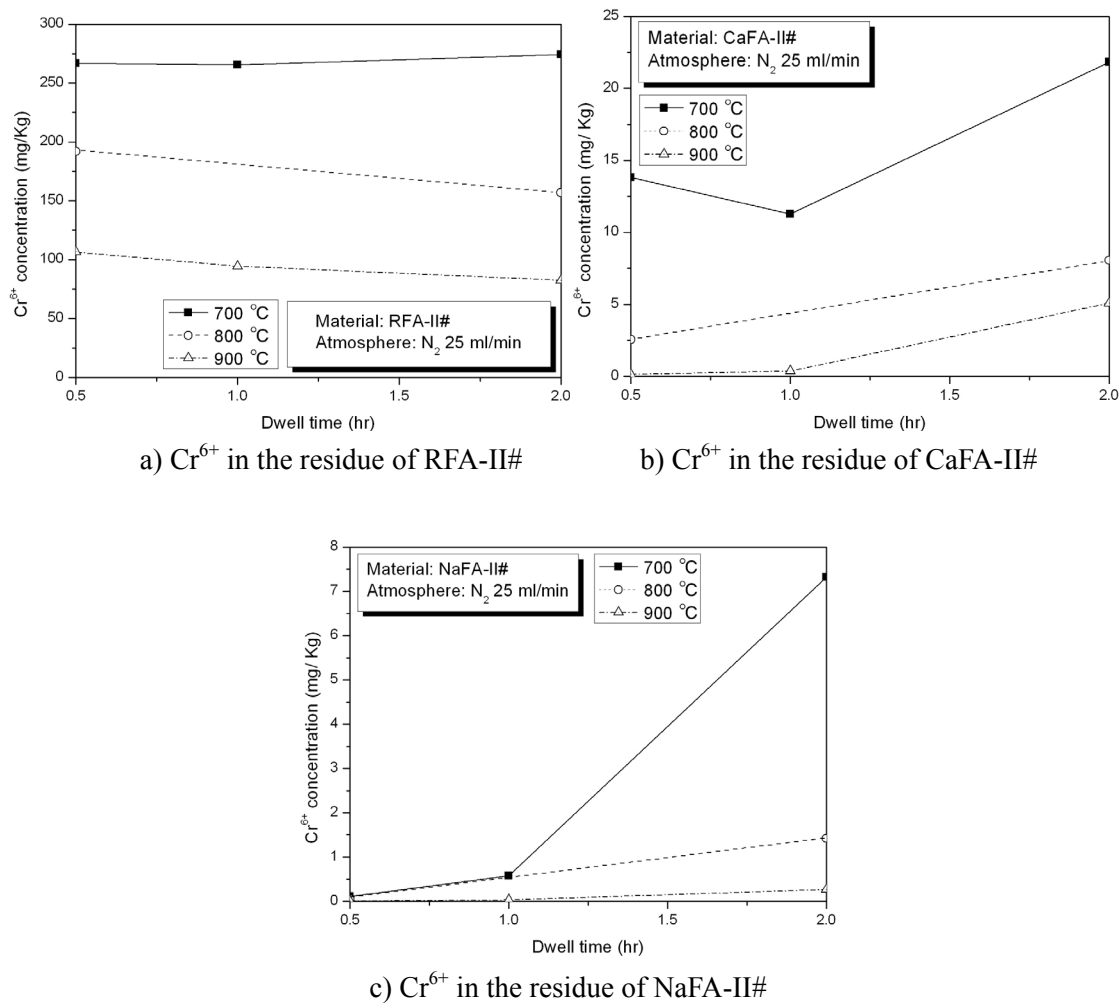


Figure 4.2 Variation of  $\text{Cr}^{6+}$  concentration in calcinating preliminary experiments

#### 4.2.2.2 Formal experiments

Based on the results of preliminary experiment and literature review<sup>9</sup>, it can be found that heating temperature is the most important parameter, so I carried out the formal experiments according to the routine as Table 4.3, 4.4 and 4.5 shows: 1) Experiment I (Table 4.3), I want to find the suitable heating temperature, so I vary the heating temperature from 400 °C to 1,100 °C. Because that temperature range includes almost all the temperature range in the MSW incinerator, and because RFA-II# will be melted at 1,200 °C and difficult to be removed from the combustion boat. I fix the other parameters as that the atmosphere is 100%  $\text{N}_2$  with 25 ml/min, the heating time and dwelling time is one hour respectively so that the total time range is not more than 2 hours; 2) Experiment II (Table 4.4), after getting the suitable heating temperature, I want to know the influence of atmosphere on calcinating process, so I change the



atmosphere from N<sub>2</sub> to 10% O<sub>2</sub> (N<sub>2</sub> for balance) and the flux is set as 25 ml/min, 50 ml/min and 75 ml/min; 3) Experiment III (Table 4.5), definitely longer dwell time is better, however, I do not know the exact difference, so as a comparison I fix the atmosphere, gas flux, and heating temperature and use only RFA-II# to discuss the influence of dwelling time. The detailed information of the formal experiments is shown in Table 4.3, 4.4 and 4.5.

Table 4.3 Experimental design of the formal experiments I

Code	Temperature (°C)	Heating time (hr)	Dwell time (hr)	Code	Temperature (°C)	Heating time (hr)	Dwell time (hr)
1#	400	1	1	5#	800	1	1
2#	500			6#	900		
3#	600			7#	1000		
4#	700			8#	1100		

Note: the atmosphere is N<sub>2</sub> 25 ml/min.

Table 4.4 Experimental design of the formal experiments II

Code	Temperature (°C)	Heating time (hr)	Dwell time (hr)	Atmosphere	Flux (ml/min)
9#	1000	1	1	10% O <sub>2</sub>	25
10#					50
11#					75

Table 4.5 Experimental design of the formal experiments III

Code	Temperature (°C)	Heating time (hr)	Dwell time (hr)	Atmosphere	Flux (ml/min)
12#	1000	1	0.5	10% O <sub>2</sub>	50

Every experiment condition was repeated for three times. Each time 5 gram sample was loaded in a combustion boat ( $14 \times 12 \times 140$  mm<sup>3</sup>).

## 4.3 Results and discussions

### 4.3.1 Discussion on heating temperature

I calculated standard deviation of LOR value for each repeated experiment. To

RFA-II#, the maximum standard deviation is 0.44%; to CaFA-II#, the maximum standard deviation is 1.05%; and to NaFA-II#, the maximum standard deviation is 0.69%. As to chlorine content, I checked it in each sample by XRF two times and then I used the average value of those two results.

Figure 4.3 presents the LOR and chlorine content of the calcinated residues.

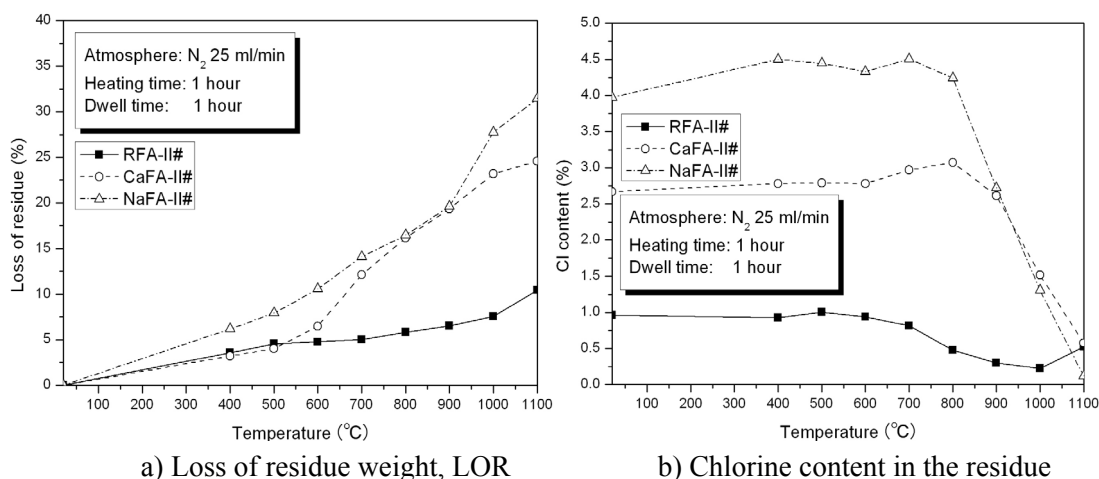


Figure 4.3 Experiment results of calcinating formal experiment I

From Figure 4.3 it can be seen that temperature has very significant impact on the LOR value and chlorine content of the calcinated product of RFA-II#, CaFA-II# and NaFA-II#, especially CaFA-II# and NaFA-II#. The LOR value continues to increase with the increasing of heating temperature. However, the chlorine content shows different performance. To NaFA and CaFA, the chlorine content gradually increases with the increasing of heating temperature from room temperature to 800°C, while, when the heating temperature is higher than 800°C, the chlorine content goes down sharply. To RFA, that turning point is around 600-700°C. The first gradual increasing might be due to the loss of other chlorine-free compounds in the residues and the latter sharp decrease could be due to the sublimation of chlorides. The detailed discussion will be carried out in the following sections.

#### 4.3.1.1 Decision on the heating temperature

Similar as I did in the research of washing condition, I will use Formula 2.3 to calculate the left derivative of the LOR curves, because that value represents the decreasing/increasing speed of “y” value, such as LOR value and/ or chlorine amount, at the corresponding point. The results are showed in Figure 4.4. As to chlorine amount

I assume that there is 100 gram of each RFA-II#, CaFA-II# and NaFA-II#, and then according to the results shown in Figure 4.3 I calculate the total amount of chlorine left in the residue after being calcinated (Figure 4.4b) as well as the left derivative of the corresponding curve (Figure 4.4c). The amount of chlorine left was calculated in Formula 4.2.

$$Cl_{left} = 100\text{gram} \times (1 - LOR) \times Cl\% \quad (4.2)$$

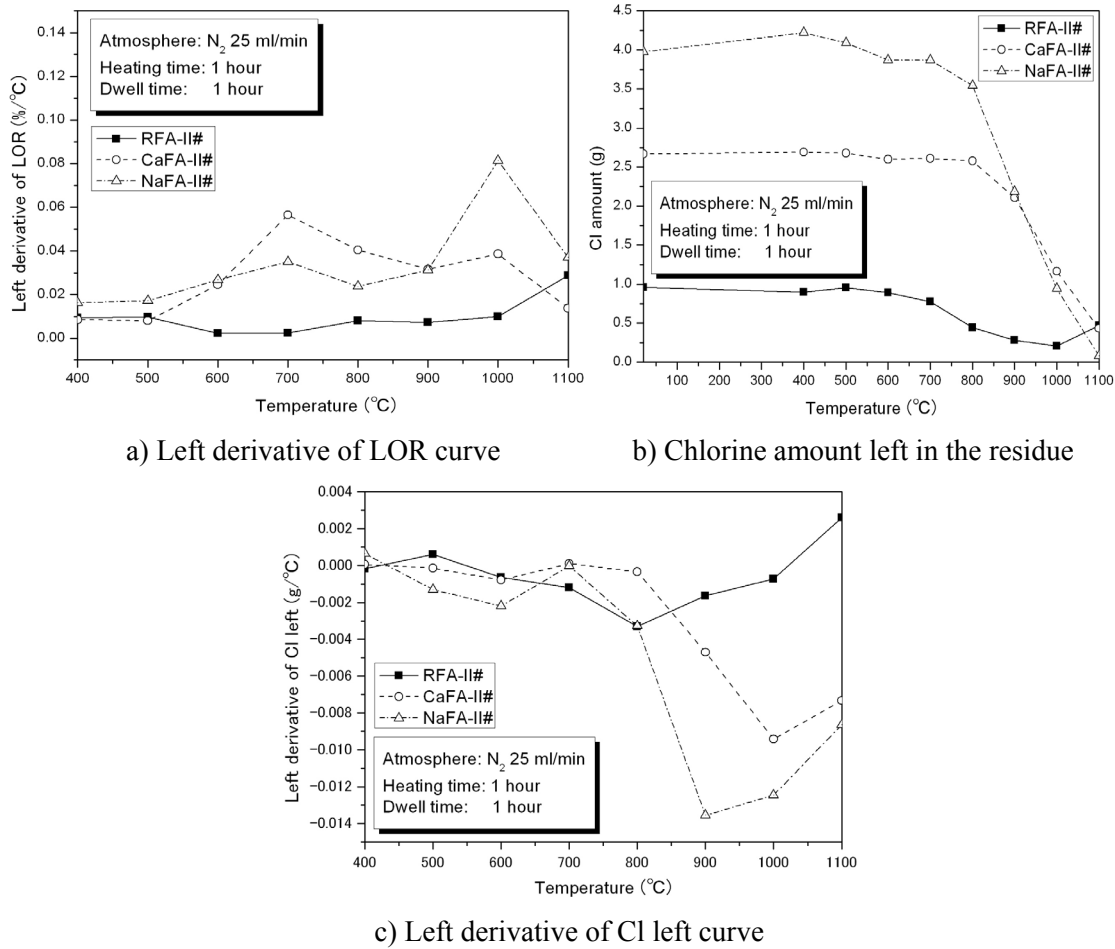


Figure 4.4 Data process from Figure 4.3

From Figure 4.4a, it can be found that in the temperature range from 400°C to 1,100°C, the maximum left derivative value of RFA-II# LOR curve happens at 1,100°C, that of CaFA-II# LOR curve is at 700°C and that of NaFA-II# LOR curve is at 1,000°C. While as to chlorine decreasing, according to Figure 4.4c, the maximum decreasing speed of RFA-II# positions at 800°C, that of CaFA-II# is at 1,000°C and that of NaFA-II# is at 900°C (The second maximum decreasing rate of the chlorine amount in

NaFA-II# positioned at 1,000°C). As a result, I set the heating temperature at 1,000°C. Certainly the loss of weight is directly related to the component in RFA-II#, CaFA-II# and NaFA-II#. As all those three samples were got from the washing experiment and dried at 105°C for 24 hours, there is thought to be some hydrates<sup>8-11</sup>, which will loss the combined H<sub>2</sub>O when the residues are heated. Another reason should be the volatilization of the compounds with low melting point or boiling point. Besides chlorine I checked the variation of the element concentration in the residues, and I noticed that the concentration of carbon decreased very fast. As a result I calculate, if 100 gram residue was heated, the lost amount of carbon,  $C_{lost}$ , and the lost amount of residue,  $R_{lost}$ , and corresponding contribution ratio of  $C_{lost}$  to  $R_{lost}$ ,  $C_{contribution}$ . The relationship among  $C_{lost}$ ,  $R_{lost}$  and  $C_{contribution}$  is described in Formula 4.3.

$$C_{contribution} = \frac{C_{lost}}{R_{lost}} \times 100\% \quad (4.3)$$

The value of  $C_{contribution}$  is shown in Figure 4.5. Obviously the loss of carbon attributes to considerable portion of the residue weight loss, especially to CaFA-II# and NaFA-II#. With the increasing of temperature, the contribution decreases slowly. That might be due to the volatilization of other compounds such as chloride.

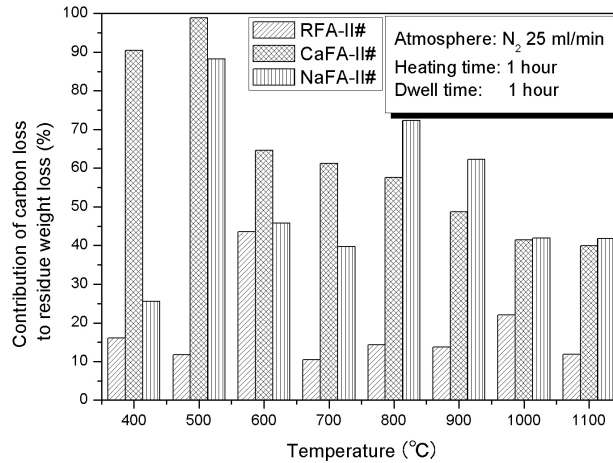


Figure 4.5 Contribution of carbon loss to residue weight loss

#### 4.3.1.2 Comparison of RFA-II#, CaFA-II# and NaFA-II#

From Figure 4.3a and Figure 4.4b, it is clear that comparing to CaFA-II#, both the loss of residue mass percent and the loss of chlorine weight percent of NaFA-II# are larger. For example, at 1,000°C, the LOR value of NaFA-II# is 27.7% and that of CaFA-II# is 23.2%, and the corresponding LOR value of RFA-II# is 7.54%. If 100 gram residue is

calcinated, the amount of chlorine left in the calcinated residue of NaFA-II# is 0.944 gram, that of CaFA-II# is 1.17 gram and that of RFA-II# is 0.209 gram. The loss of chlorine weight percent of those three kinds of residues can be defined as Formula 4.4, so the corresponding values of NaFA-II# and CaFA-II# are 76.2% and 56.3% respectively, while that of RFA-II# is 78.2%.

$$\frac{Cl_{origin} - Cl_{left}}{Cl_{origin}} \times 100\% \quad (4.4)$$

From this point, the injection of  $\text{NaHCO}_3$  has more positive influence on reducing chlorine amount in calcinating process than the injection of  $\text{Ca(OH)}_2$ , because the washed residue from NaFA (NaFA-II#) is easier to release chloride than the washed residue (CaFA-II#) from CaFA. This might be the existing status of chlorine in CaFA-II# is different from that of chlorine in NaFA-II#, so do other components. For example, in Chapter 3, it was found that chloride speciation in CaFA-II# is different from that in NaFA-II#, and there are more calcium chloride and insoluble chlorides in CaFA-II# than in NaFA-II#.

#### 4.3.2 Discussion on atmosphere and corresponding flux

Figure 4.6 shows the LOR value and chlorine content results of formal experiments II. I also includes the results of RFA-II#-7#, CaFA-II#-7# and NaFA-II#-7# in formal experiments I to compare.

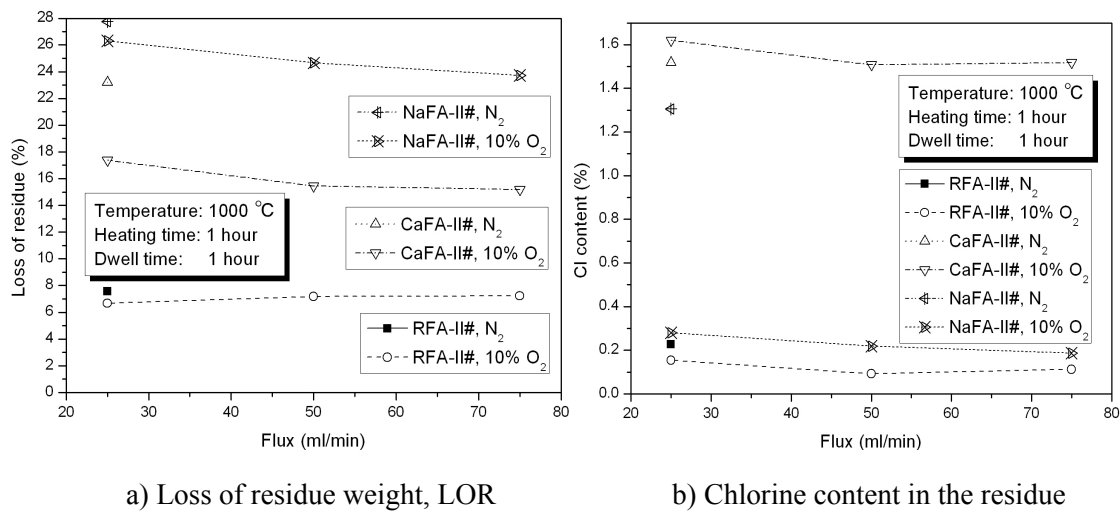


Figure 4.6 Experiment results of formal experiment II

The LOR value under the condition of pure N<sub>2</sub> gas atmosphere is always larger than that under the condition of 10% O<sub>2</sub> gas atmosphere, especially to CaFA-II#. While, as to chlorine content, the situation is opposite to RFA-II# and NaFA-II#. 10% O<sub>2</sub> has better influence on removing chloride out from RFA-II# and NaFA-II# than N<sub>2</sub>, especially to NaFA-II#. For CaFA-II#, pure N<sub>2</sub> gas is better than 10% O<sub>2</sub> gas (90% N<sub>2</sub> as balance) to reduce chlorides. However, that predominance is not so obvious. As a result, I chose 10% O<sub>2</sub> (90% N<sub>2</sub> as balance) as the atmosphere for experiments.

I varied the flux of atmosphere gas of 10% O<sub>2</sub> at 25 ml/ min, 50 ml/ min and 75 ml/ min. From Figure 4.6, as to LOR value of RFA-II#, larger flux is better and the maximum value happened at 75 ml/min. As to LOR value of CaFA-II# and NaFA-II#, the situation is opposite and smaller gas flux is better with the maximum LOR value at 25 ml/ min. Among the current flux range, the influence of gas flux on reducing the amount of residue and chlorine is not very obvious. As to the chlorine content in the final residue, RFA-II# and CaFA-II# have the minimum chlorine content at 50 ml/ min, while NaFA-II# is at 75 ml/ min. So at last I decide to adopt 50 ml/ min 10% O<sub>2</sub> (90% N<sub>2</sub> as balance).

As to the reason why O<sub>2</sub> gas can accelerate the reduction of chlorides in residue, it is thought that oxygen atom will replace chlorine in some compounds, because the ability of oxidation of oxygen is stronger than that of chlorine. However, that influence is not so obvious according to the results.

O<sub>2</sub> gas will certainly change the status of Cr in the residue, so I checked the concentration of Cr<sup>6+</sup> in the residues. Figure 4.7 shows the results. In order to compare, I also includes the results of RFA-II#-7#, CaFA-II#-7# and NaFA-II#-7#. The influence of O<sub>2</sub> on the production of Cr<sup>6+</sup> in the residue is positive, especially to RFA-II#, then CaFA-II# and the last is NaFA-II#. From this point, NaFA-II# calcinated is safer than CaFA-II# calcinated, however, long dwell time is not good for NaFA-II#.

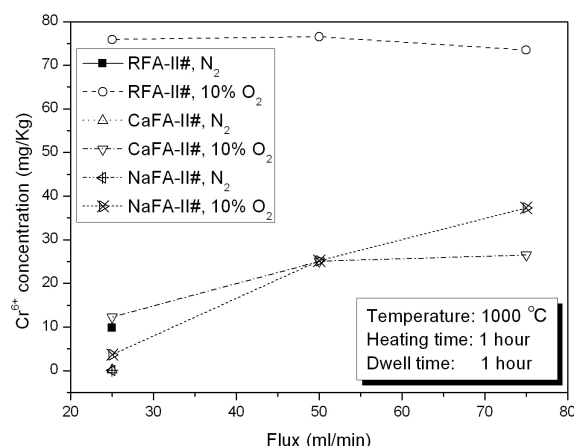


Figure 4.7 Cr<sup>6+</sup> concentration in the residues of formal experiments II

### 4.3.3 Discussion on dwell time

I have discussed in the preliminary experiments that dwell time is less important than heating temperature to reduce the amount of residue and chlorine content. According to literature reviews <sup>8, 9</sup>, normally the longest dwell time is 2 hours. Now in formal experiments I and II, both the heating time and dwell time are set as 1 hour. From the results in formal experiments I, I know that since 400°C there is change in the residue weight and chlorine content, so the heating method of heating for one hour and dwelling for one hour equals to the heating method of dwelling than one hour longer but less than 2 hours. Longer time is not so necessary, nor is too short time. So I only tried one experiment by changing the dwell time from 1 hour to 30 minutes, fixing the heating and dwelling temperature at 1,000°C, using atmosphere as 10% O<sub>2</sub> (90% N<sub>2</sub>). RFA-II# was chosen as the experiment material. The result is presented in Table 4.6. In order to better comparison I includes the result of RFA-II#-10#.

Table 4.6 Experimental results of the formal experiments III

Code	LOR (%)	Chlorine content (%)	Cr <sup>6+</sup> (mg/ Kg)	Dwell time (hr)
10#	7.18	0.0921	76.5	1
12#	6.70	0.262	81.1	0.5

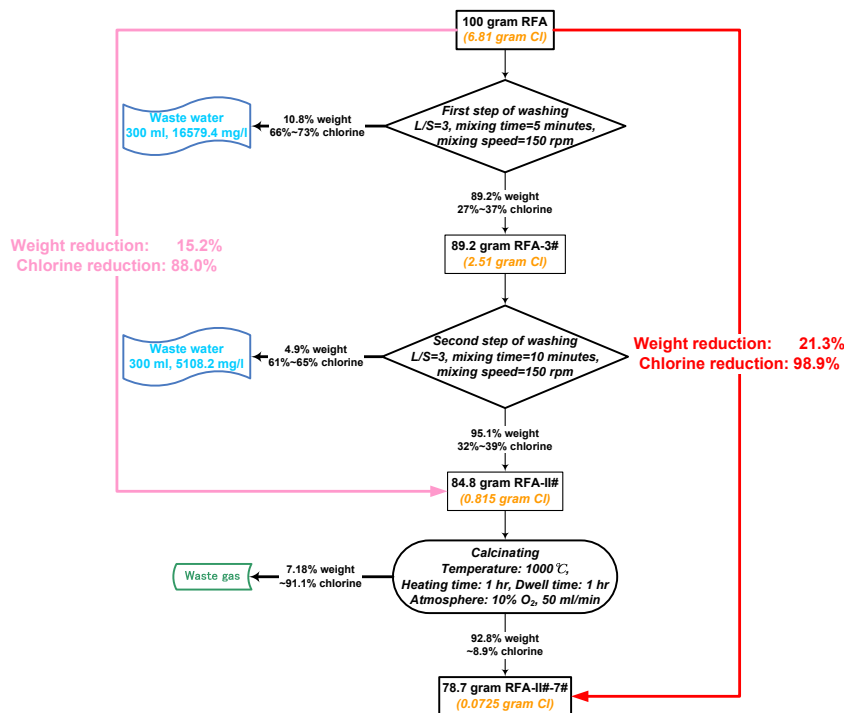
\* As to experiment condition, please refer to Table 4.4 and 4.5

Obviously the dwell time of 1 hour has better results than dwell time of 0.5 hour. The chlorine amount left in the residue of RFA-II#-10# is 0.0855 gram, if 100 gram

RFA-II# is treated under the 10# experiment condition, while chlorine amount left in the residue of RFA-II#-12# is 0.244 gram, which is almost three times of that in the residue of RFA-II#-10#. Also the concentration of  $\text{Cr}^{6+}$  in the residue of RFA-II#-10# is less than that in RFA-II#-12#. So at last I decide to use the dwell time as one hour. In all, I decide the final experiment condition for calcinating is that heating time is 1 hour, dwell time is one hour, temperature is  $1,000^{\circ}\text{C}$  and the atmosphere is 10%  $\text{O}_2$  at 50 ml/min. To choose that condition is just based on the current results in calcinating process with the aim to reduce chlorine content. In the future, when considering the WCCB system in whole with the aspects of energy and cost, that condition possibly will be changed, so does the condition of washing process.

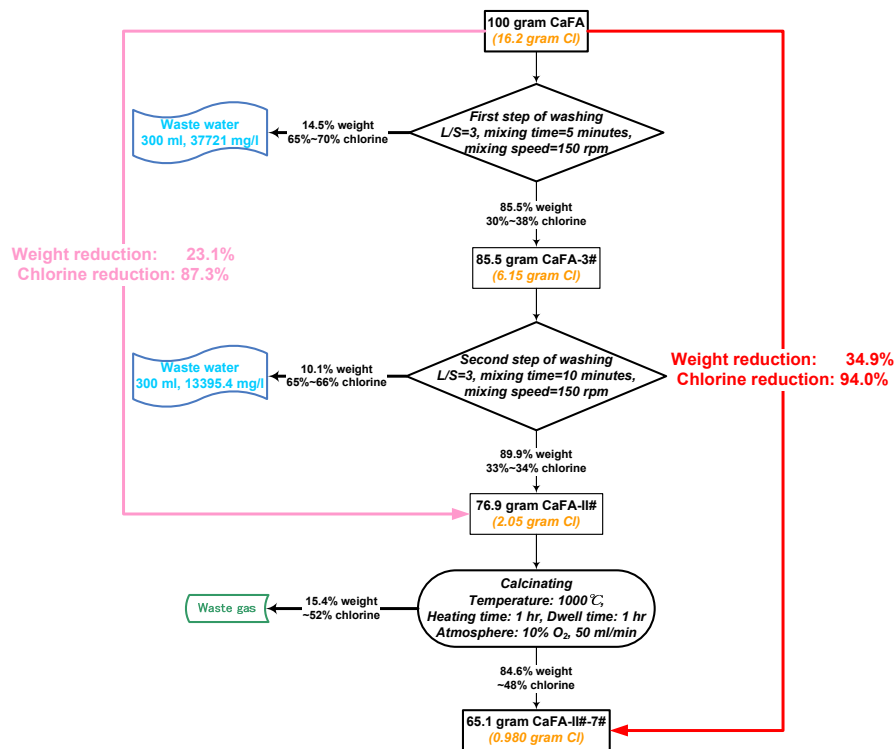
#### 4.3.4 Chlorine flow of WCCB system

After I decided the final condition for calcinating process, together with the condition for washing process, I can calculate the chlorine flow from washing to calcinating. Figure 4.8 shows the detailed information.

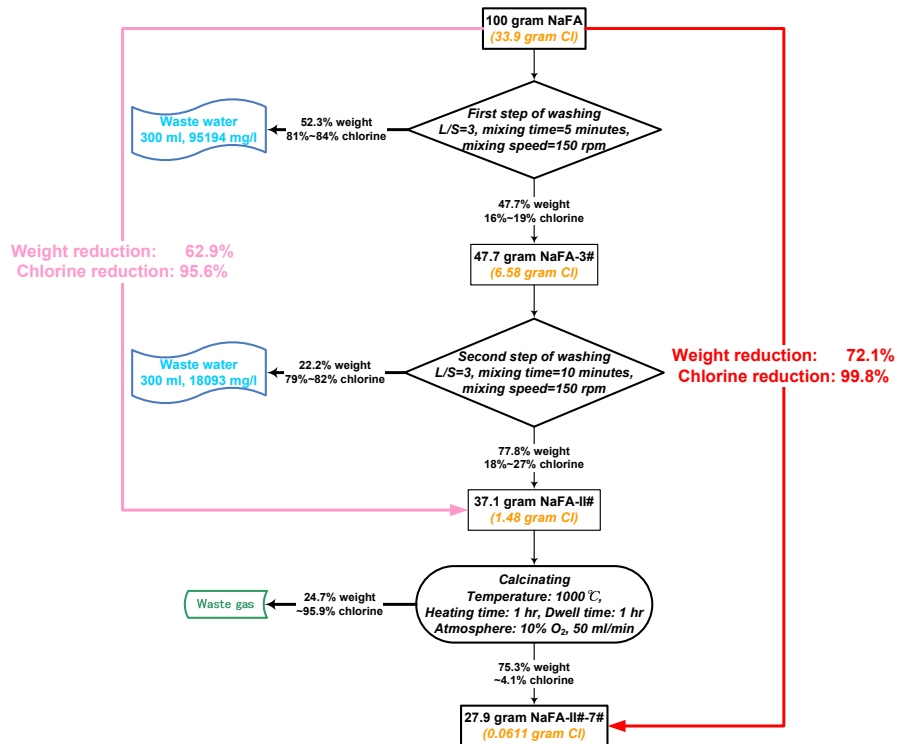


a) Chlorine flow in RFA from washing to calcinating





b) Chlorine flow in CaFA from washing to calcinating



c) Chlorine flow in NaFA from washing to calcinating

Figure 4.8 Chlorine flow in fly ashes from washing to calcinating

From Figure 4.8 I can conclude that “washing + calcinating” is effective to reduce the amount of fly ash and chlorine, especially to NaFA. Calcinating is not so effective to reduce the amount of washed fly ash, but it is good to reduce the chlorine in the washed fly ash, for example, relative to RFA-II#, about 91% chlorine can be reduced by calcinating, relative to CaFA-II#, about 52% chlorine can be reduced and relative to NaFA-II#, about 96% chlorine can be reduced. So calcinating process is also necessary. Figure 4.8 also clearly shows the superiority of NaFA over CaFA in mass reduction and chlorine reduction.

To evaluate the importance of washing process, I heated RFA, CaFA and NaFA under the condition I decided for calinating process. The LOR value of RFA is  $12.0 \pm 1.4\%$  and chlorine content is 3.72%. As to the case of CaFA, the LOR value changed with time range that I put the sample open to the air after it was calcinated. It is possibly due to the big portion of  $\text{CaCl}_2$ , which is very hygroscopic. The chlorine content in the calcinated residue of CaFA is 16.8%, which is checked by XRF. Comparing the results with those of the corresponding washed residue, washing is a necessary step to reduce chlorides. As to NaFA, at that condition, it was melted. It seems that washing process had removed the compounds of low-melting point out from NaFA.

#### 4.4 Conclusion

From the experiment results, I can conclude that calcinating is an important step of WCCB system. It can reduce 91% chlorine from washed residue of RFA, 52% chlorine from washed residue of CaFA and 96% chlorine from washed residue of NaFA. It should be the different chloride speciation among those residues.

In preliminary experiments, it was found that heating temperature was more important than dwell time. Based on that, I designed the formal experiments to discuss the influence of heating temperature, atmosphere and dwell time step by step. At last I decided one condition for calcinating process: heating temperature is  $1,000^\circ\text{C}$ , heating time is 1 hour, dwell time is 1 hour, and atmosphere gas is 10%  $\text{O}_2$  (90%  $\text{N}_2$ ) at the flux of 50 ml/min.

The experiment results of both preliminary experiments and formal experiments show that the washed residue of NaFA can be reduced 24.7% by weight, while that of CaFA can be reduced only 15.4%. As to chlorine decrease, the data of the washed residue of NaFA is 95.9%, while that of CaFA is 52%. So I can get the similar conclusion as in washing process that NaFA is better than CaFA to be recycled.

Calcinating process is at least as complex as washing process or even more complicated. I normally thought pure  $N_2$  might be better than  $O_2$  to reduce the amount of residue and chlorides, because oxides usually have higher melting point or boiling point than the corresponding chlorides. However, the result was not all like that. The result is that  $O_2$  gas showed positive influence on the reduction of chloride in RFA and NaFA, but negative on CaFA.

In this research I mainly concerned about the reduction of chlorine and a little about  $Cr^{6+}$ . I had better do more research about the behavior of other factors such as dioxins, leaching characteristics of Pb and other heavy metals, also, I have to take the issue of energy and cost into account, so that I can evaluate and optimize the whole WCCB system in comprehensive and truly environmentally friendly way.

## 4.5 References for Chapter 4

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## 5 CONCLUSION

This is the last chapter for this dissertation. In this chapter I will summarize briefly the research content and main results in the former chapters.

### Chapter 1

In Chapter 1, I first explained the serious situation of the problem of environment, and then I put forward the problem of municipal solid waste. As one of the most important treatment, incineration is very popular in Japan and some European countries. However, incinerator still has second pollutions such as fly ash, bottom ash and discharged gas, and other troubles. So to find out a more environmentally management system for incineration is critical for Sound Material-Cycle Society. After having an comprehensive review for the current treatments for fly ash and our former research, I proposed a new recycling system for fly ashes——“WCCB”. “W” means washing; the first “C” means calcinating; the “CB” means changing the treated fly ash with bottom ash into raw material in cement industry. The detailed technology flow is in Figure 1.4. I mean to use WCCB system to minimize the amount of fly ash discharged out of the whole system and maximize the recycling ratio of fly ashes as the raw material in cement industry. As a result, there are two purposes for our research. According to 3R principals, the first purpose is to cut down the amount of residue as much as possible, and because of the high limitation for chlorine content in cement industry, to reduce the chlorine content in the fly ash is another important purpose. In WCCB system, I also tried the fly ash gathered from the bag filter resulting from the neutralizing the acid compound in discharged gas by injecting  $\text{NaHCO}_3$ . From comparing the results of that fly ash resulting from injecting  $\text{NaHCO}_3$  (NaFA) with the fly ash resulting from injecting  $\text{Ca(OH)}_2$  (CaFA), I am able to optimize the WCCB system in another aspect, which is to use new alkaline reagent. So including the raw fly ash from the boiler (RFA), I will discuss three kinds of fly ash in this research: RFA, CaFA and NaFA.

## Chapter 2

In Chapter 2, I started the research of washing process in WCCB system. In this chapter, I mainly concerned about the most suitable parameters for washing process. Based on the literature review and our preliminary experiments results, I designed the formal washing experiments for all the three kinds of fly ashes. I first carried out single washing experiments, then double washing experiments and last triple washing experiments. Triple washing experiments conditions were designed according to the results of double washing experiments, while double washing experiments conditions were set referenced to the results of single washing experiments. In the washing experiments it was found that washing frequency is more important than liquid to solid ratio, mixing time and mixing speed to reduce the amount of residue and chlorides in fly ash. In addition of reducing residue mass and chloride amount, I also thought about problems of energy, consumption time. At last I decided one condition for washing process: double washing and the detailed parameters are that liquid to solid ratio is 3 at the first and second step, mixing speed is 150 rpm at both step, and mixing time is 5 minutes in the first step and 10 minutes in the second step. Just as what other researchers have discovered that washing is effective to remove chloride content, our experiments showed the similar trend: about 88% chlorine in RFA, about 87.3% chlorine in CaFA and 95.6% chlorine in NaFA can be removed by washing process. With the results from washing experiments, I also compared the difference between CaFA and NaFA. It is obviously that NaFA is better than CaFA at mass reduction and chloride reduction. For example, the amount of NaFA could be reduced 62.9% through the washing experiment with the decided parameter, while that value of CaFA is only 23.1%. Less residue amount is more beneficial, because after all waste is waste, there are negative factors, and less residue amount will consume less energy in the next step. The same trend happened in the chloride reduction. Another aspect is that the neutralization efficiency of  $\text{Ca}(\text{OH})_2$  is lower than that of  $\text{NaHCO}_3$ , which resulted in more CaFA than NaFA with the same condition of discharged gas. So in all I recommend to use  $\text{NaHCO}_3$  as the neutralization reagent instead of  $\text{Ca}(\text{OH})_2$ .

## Chapter 3

In Chapter 3, I meant to explain the chloride reduction mechanism of washing experiments. In order to do this, I first have to do a speciation analysis of chlorides in those three kinds of fly ashes and the corresponding residues from the washing

experiments. There is few literature that have reported the detailed information of that except using washing experiment to deduce how much chlorides are soluble or insoluble or using X-ray diffraction (XRD) to identify the existence of some chlorides. So I explored a new method of combining X-ray near edge structure (XANES) with XRD to do the speciation analysis. I summarize the deduction methods in the following content.

#### *Identification approach*

First, reference chlorides were chosen based on the element content of the three fly ashes and a literature review. Second, by comparing the chlorine K-edge XANES spectra of fly ashes and those of reference chlorides and by examining the washing experiment results, I excluded some chlorides from LCF analysis to produce a list of “possible reference chlorides.”

After verifying the reliability of LCF method in this research, I discussed the chloride chemical form found in RFA, CaFA, and NaFA separately. I first showed the XRD spectra of fly ash and samples from the washing experiment. Based on the relationship among RFA, CaFA, and NaFA, I then separated the “possible reference chlorides” into three groups: A) chlorides that must be in fly ash, identified by the XRD spectra of fly ash; B) chlorides that have a high possibility of being in fly ash, as determined by XRD spectra of samples from washing experiments; and C) chlorides less likely to be in fly ash, i.e., the remaining chlorides.

Lastly, I finalized the “A” group chlorides and selected one or two additional chlorides from the “B+C” group for LCF analysis. I chose the combination with the lowest R value and used the results from previous research to verify that combination as well as the corresponding distribution of chlorides. A diagram of the analysis procedure is available in Figure 3.2.

#### *Chloride speciation analysis for three kinds of fly ashes*

With the identification methods I successfully processed the speciation analysis of RFA, CaFA and NaFA.

#### *Chloride behavior in washing process of three kinds of fly ashes*

Also I applied that method to the residues from washing experiments so that I can study the chloride behavior in the washing experiments. By comparing the chloride behavior in the residues of CaFA and those in NaFA, I concluded that NaFA is more suitable to be the raw material in cement industry, because under the same condition



both the total amount of left chlorine and that of the chlorine in insoluble chlorides in the residues of NaFA are less than that in CaFA as well as the chlorine in  $\text{CaCl}_2$  related form, which is more dangerous to cement than NaCl and KCl. Another result is that the insoluble chlorides in both CaFA and NaFA changed during the washing process. They are strongly related to  $\text{CaCl}_2$  and will release some  $\text{CaCl}_2$  during the washing process. Double washing is effective to remove soluble chlorides. As to insoluble chlorides, the influence is not so obvious. The analysis of chloride speciation in residues from RFA washing experiments shows the similar trends that double washing is more significant than single washing, and the insoluble chlorides in RFA is strongly related to  $\text{CaCl}_2$ , which will be released during the washing process.

## **Chapter 4**

In Chapter 4, I discussed the calcinating condition for the residues from the washing process. I adopted the same procedure as I have done in the study of washing process. Firstly, I carried out the preliminary experiments to find out the hierarchy of the parameters of calinating experiments such as temperature, heating time, dwell time and atmosphere. The results of preliminary experiments show that temperature is more critical than other factors to influence the final results of calcinating. Then I designed the formal experiment condition in three parts.

### *Discussion on temperature*

I testified the temperature from  $400^\circ\text{C}$  to  $1100^\circ\text{C}$ . The residue mass goes down when the temperature rises, which is more obvious to CaFA and NaFA when the temperature is higher than  $600^\circ\text{C}$ . I deduced there were about three factors contributing to the loss of residues. One is the decomposition of some hydrates in the washed residues, the other is the loss of carbon and the last is the vapor or sublimation of compounds of low melting point and boiling point, which includes most of chlorides. However, the variation of chlorine concentration in the residues is different from that of residue mass. When the temperature is higher than  $700^\circ\text{C}$ , the chlorine concentration goes down sharply. While,  $1000^\circ\text{C}$  is the point that the decreasing speed of chlorine content or amount becomes slower. So I decided  $1000^\circ\text{C}$  as the heating temperature.

### *Discussion on atmosphere*

In this part I compared the results under the condition of 100%  $\text{N}_2$  at 25 ml/min, 10%  $\text{O}_2$  (90%  $\text{N}_2$ ) at 25 ml/min, 50 ml/min and 75 ml/min. To RFA and NaFA, 10%  $\text{O}_2$  is

more positive to reduce the mass residue and chlorine, especially to NaFA. While to CaFA, 10% O<sub>2</sub> seems a little negative, however, it is tiny. More over, it was found that the result under the condition of 10% O<sub>2</sub> at 50 ml/min was better. As a result, the final condition decided is that heating temperature is 1000°C, heating time is 1 hour, dwell time is 1 hour and atmosphere is 10% O<sub>2</sub> at 50 ml/min. Under that condition the residue mass of washed residue of RFA can be reduced 7.18%, that of CaFA can be reduced 15.4% and that of NaFA can be reduced 24.7%. As to chlorine amount, about 91% in the washed residue of RFA can be removed, 52% chlorine in the washed residue of CaFA can be removed and 95.9% chlorine in the washed residue of NaFA can be removed. So from the above data I also conclude that NaFA has superiority than CaFA at the mass reduction and chloride reduction.

#### *Discussion on dwell time*

Because of the characteristics of the heating tube, to skip the step of heating phase is difficult. And normally the dwell time is not longer than 2 hour, so I tried only one other condition for the washed residues of RFA to see the influence of dwell time. I shortened the dwell time from 1 hour to 0.5 hour and kept the heating time as 1 hour, heating temperature as 1000°C, atmosphere as 10% O<sub>2</sub> at 50 ml/min. The result shows that longer dwell time is better to reduce the residue weight percent and chlorine content, especially chlorine content.

#### **Recommendation for future research**

I have set up a relatively reasonable recycling system for fly ash——WCCB. Based on our research, considering the residue weight reduction and chloride reduction as well as energy and consumption time, I chose the most acceptable condition for washing process and calcinating process. The final condition for washing process is that liquid to solid ratio is 3 at the first and second step, mixing speed is 150 rpm at both step, and mixing time is 5 minutes at the first step and 10 minutes at the second step. The final condition for calcinating process is that heating temperature is 1000°C, heating time is 1 hour, dwell time is 1 hour, and the atmosphere is 10% O<sub>2</sub> (90% N<sub>2</sub>) at 50 ml/min. I also successfully explained the chloride reduction mechanism in washing experiments. With all the research I conclude WCCB system is the promising system for recycling fly ash, and NaHCO<sub>3</sub> is better than Ca(OH)<sub>2</sub> to be used as alkaline reagent to neutralize the acid compound in discharged gas from the view of recycling.

However, in my doctor dissertation, I studied WCCB system mainly from the technological factors. If WCCB system is required to be applied into practice, some

work is necessary. The other work can be a comprehensive evaluation, which includes the calculation of the cost and energy consumption, the evaluation of environmental risk and impact, and their interrelationship. Based on that comprehensive evaluation, it is possible for us to choose proper operating conditions for what I prefer. In order to fulfill a successful evaluation, I would recommend some possible tasks to be done:

- a) It is better to process the WCCB system under two or three sets of operating parameters for further analysis and comparison.
- b). Make a mass balance study of WCCB system under each set operation parameters of WCCB system. The concerned elements can be chlorine, sulfur, sodium, potassium, calcium, copper, zinc, iron, lead and chromium.
- c). Detect the behavior of other poisonous compound such as dioxins in WCCB system.
- d). Process a risk evaluation for environment. Based on the research in the second and third step, I will have gathered the basic information to do a risk evaluation of WCCB system in the view of environmental impact.
- e). Make energy and economic analysis.
- f). Optimize the operation factors of WCCB system.

After the above steps were finished, I am supposed to obtain the following results or achievement: 1). A practical welcomed WCCB system for fly ash from municipal solid waste incinerator (MSWI). And I can apply it to the waste which has similar characteristics as fly ash from MSWI; 2) A model to simulate and optimize WCCB system; 3) A revolution on the use of the neutralization reagent in MSWI. Neutralization reagent in sodium compounds is possibly to substitute the traditional calcium compounds; 4) A good resource for urban mine; 5) A good example for the Sound Material-Cycle Society.

WCCB system is more than a recycling system for fly ash. I can apply it to other solid wastes with similar characteristics such as the ash from the electric power production industry, which consumes coal to produce electricity, the ash from the steel industry and so on. Also I can adopt the concepts in WCCB system to choose better additive in the corresponding industry, for example, in incinerator I prefer  $\text{NaHCO}_3$  than  $\text{Ca(OH)}_2$ , while in treatment of discharged gas of power industry, similar question also exists. So WCCB system has a broad application field.

## ACKNOWLEDGEMENT

Three years' doctor course in Kyoto university of Japan is a very precious experience for me.

Here, I successfully finished my doctor course in 3 years and until now I have one paper accepted by Environmental Science & Technology and one paper accepted by Waste management respectively, another one more paper submitted to Journal of the Air and Waste Management Association. To me, I am satisfied with those achievements I have got, though there is still a lot of work left to do.

At the beginning, I would express my thanks to Professor Tsuno, Professor Morisawa and Professor Sakai for reviewing my doctor dissertation and giving me valuable suggestions so that I can finish this dissertation in better quality.

Looking back on how it was in the three years gone by, in spite of my own effort and fortunate, I owe thanks to many people and I would like to express my grateful feeling to them here.

First of all I would say thanks to Professor Wang in Tsinghua University of China, without his recommendation, there might be no chance for me to enter Kyoto University. More important I would thank Professor Takeda and Professor Tsuno, their agreements made my application to Kyoto University become reality. And in the past years they have given me important guide and care. Also I would thank Professor Morisawa, since April, 2007, he began to take charge of the lab of Environmental Design Engineering. His kindness impressed me and helped me a lot.

Next I would show my grateful thanks to my direct supervisor, associate professor Takaoka. I can feel his worrying about my graduation and having arranged many things. He spent considerable time discussing my papers and research. I learned a lot from him such as more serious attitude to science and special polite to just keep silence. I can see his happiness when my paper were accepted especially the paper submitted to ES&T. I am also very excited that he would be satisfied with my job. To make supervisor think I am his pride is one of my dreams. I wish I could do more and better job to show my thanks in practical way.

I would say my thanks to assistant professor Matsumoto, assistant professor Oshita and assistant professor Hidaka. They helped me to be used to the life in Kyoto University better and quicker. I would say thanks to Mr. Shiota. He gave me a lot of help of

operating machines and taught me the skills. He was always kind. I would thank Mr. Furutuki, Miss Sakurai, Mr. Fujimori, Miss Hashimoto and Mr. Ogasahara. They all contributed to my research in different way. There are many other teachers and students who helped me in the past three years, but I can not list their name here one by one. I just want to say thanks to all the people in the lab of Environmental Design Engineering and Water Environmental Engineering. Thanks a lot!

I would also thank many chinese friends here, who makes me think I just live in China. Last but not the least, in fact it is the most important. I would thank to my family. To my husband, I would say it might be unbelievable to others that my husband would suggest me to go to Japan and I agreed. We seem have abandoned each other and in fact the first 2 years were really hard for us two. However, we struggled and supported each other in our own way and this status might have to be maintained for longer. I wish our marriage and sense will be stronger and stronger. To my mother, I owe too much thanks. In spite of your bringing me up seriously, full of love, you now take care of my husband just like your own son, which makes my husband can put all his heart into his job and so reduced some of my sorry to my husband. If all the legends are true, let me be the person who scarifies most to you from the next beginning of your life. To my father who left us almost 5 years ago, I would say do not worry about me and mother. Now I have finished the doctoral degree the last step for student, probably is the wish you never spoke to me. Be peace.

# APPENDIX

## Appendix No.1

Table A-1 experiment results of CaFA, NaFA and RFA double- and triple washing (%)

Code	CaFA		NaFA		RFA		Code	CaFA		NaFA		RFA	
	R	Cl	R	Cl	R	Cl		R	Cl	R	Cl	R	Cl
9#	74.3	1.76	39.4	1.79	86.2	0.854	17#	76.9	1.97	39.3	2.35	85.3	0.830
10#	74.2	1.82	39.6	1.78	85.4	0.815	18#	76.0	1.86	39.0	2.91	84.8	0.744
11#	73.5	1.48	37.7	1.45	84.8	1.00	19#	75.7	1.67	38.0	1.99	84.3	0.781
12#	72.2	1.08	37.0	1.45	82.7	0.677	20#	74.0	1.26	37.5	1.49	82.6	0.647
13#	74.8	1.91	37.9	2.03	85.1	0.889	21#	76.3	1.85	37.9	1.60	85.2	0.817
14#	74.6	1.54	36.9	1.78	84.0	0.716	22#	75.5	1.59	37.5	1.55	84.6	0.726
15#	74.1	1.60	38.1	1.65	83.1	0.752	23#	74.9	1.45	36.7	1.44	83.8	0.723
16#	73.3	1.22	34.6	1.50	81.8	0.655	24#	74.0	1.32	36.1	1.35	83.0	0.687
25#	72.3	1.61	35.7	0.90	83.3	0.610							

※ “R” stands for “residue weight percent”; “Cl” means the chlorine content

## Appendix No.2

### Making Friedel’s salt

Figure A-1 illustrated the procedure to making Friedel’s salt. During that process, we found that it took less time to get pure  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$  in higher heating temperature, especially  $1350^\circ\text{C}$ . In the incinerator,  $900^\circ\text{C}$  is the normal temperature in the after burning zone or secondary combustion chamber, and in some places the temperature might be higher than  $900^\circ\text{C}$  or  $1000^\circ\text{C}$ . The heating process can be fulfilled in the incinerator, as there is sure to be CaO and  $\text{Al}_2\text{O}_3$ . As to the second step of mixing  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$  with  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  and water, because the water content in the original MSW is considerable, in gas quenching tower quick cooling of discharged gas will lead to a lot of water produced.

As a result, we think the existence of Friedel's salt is of high possibility.

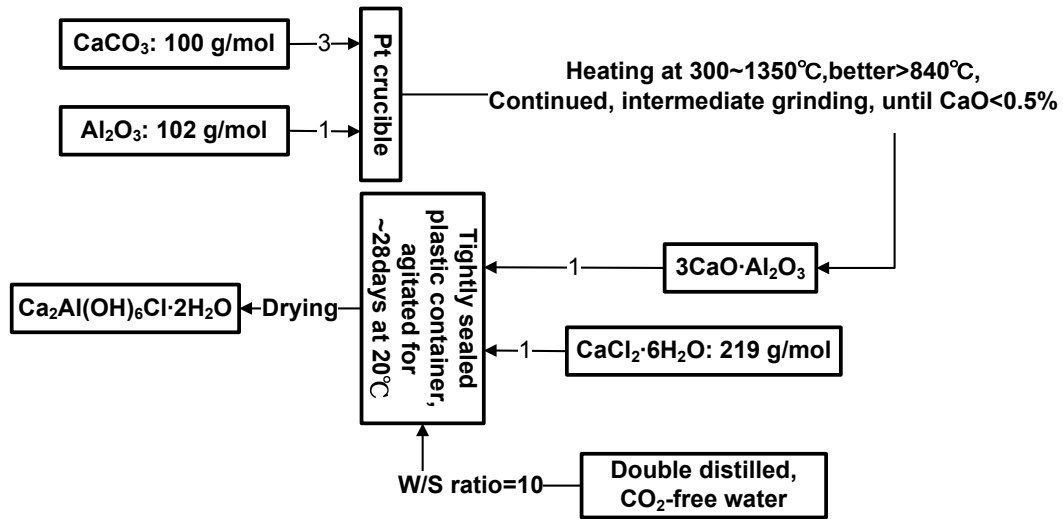


Figure A-1 The procedure for making Friedel's salt

#### Making Calcium chloroaluminate ( $11\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \cdot \text{CaCl}_2$ )

Figure A-2 illustrated the procedure of making Calcium chloroaluminate ( $11\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \cdot \text{CaCl}_2$ ). It seems easier to get calcium chloroaluminate than Friedel's salt. However, calcium chloroaluminate will decompose when temperature is higher than  $670^\circ\text{C}$ .  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$  is more stable. That is the reason why the insoluble chlorides in fly ashes are closer to Friedel's salt.

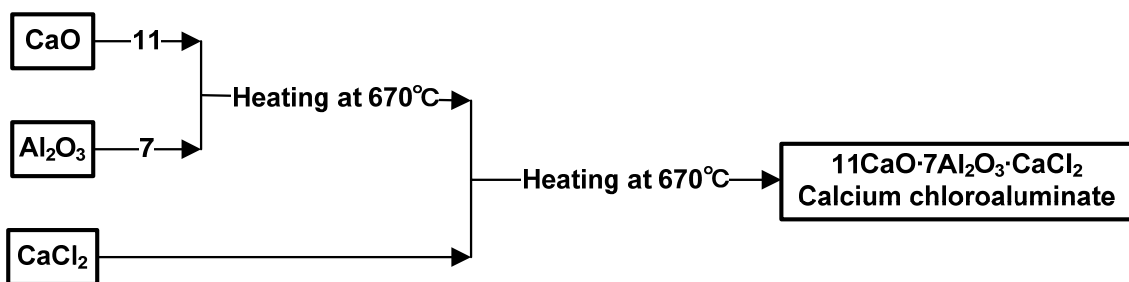


Figure A-2 The procedure for making calcium chloroaluminate

#### Making gehlenites ( $\text{Ca}_2\text{Al}_2\text{SiO}_7$ )

Figure A-3 illustrated the procedure of making Gehlenites ( $\text{Ca}_2\text{Al}_2\text{SiO}_7$ ), because in the XRD spectra of RFA and CaFA we found the existence of gehlenites ( $\text{Ca}_2\text{Al}_2\text{SiO}_7$ ,  $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ ), which has the structure of  $2\text{CaO} \cdot \text{Al}_2\text{O}_3$ .

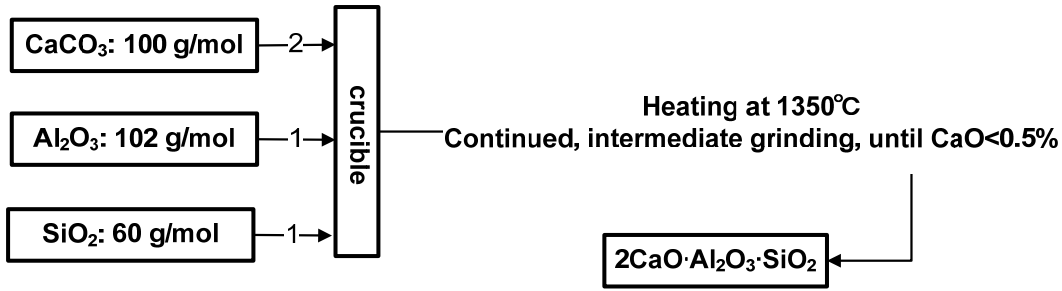
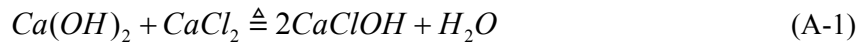


Figure A-3 The procedure for making gehlenite

The heating condition is very similar as that of  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ , but it need a little longer time than the time to make  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ . Since we can find gehlenite, the production of  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$  is very possible, so is Friedel's salt.

### Making Calcium hydroxychloride ( $\text{CaClOH}$ )

We made calcium hydroxychloride ( $\text{CaClOH}$ ) according to Formula A-1. The heating temperature is around  $200^\circ\text{C}$  for about 2 hours, and then we can check out the peaks of  $\text{CaClOH}$  by XRD. The temperature in bag filter is around  $200^\circ\text{C}$ , and the time range, from the calcium hydroxide was injected into the pipe of the discharged gas to that the mixture arrives at bag filter and is caught by bag filter, is enough to get  $\text{CaClOH}$ . Other researchers also verified it<sup>16, 17</sup>.



### Appendix No.3

The following content presented the calculation process of the element molar ratio among RFA and among all the chlorides in RFA.

$$m_{[\text{Ca}_2\text{Al}(\text{OH})_6]\text{Cl} \cdot 2\text{H}_2\text{O}} = 24.6\% \Rightarrow \begin{cases} m_{\text{Ca}, \text{Cl}, \text{F}} = 24.6\% \times 2 = 49.2\% \\ m_{\text{Al}, \text{Cl}} = 24.6\% \end{cases} \quad (\text{A-2})$$

$m_{[\text{Ca}_2\text{Al}(\text{OH})_6]\text{Cl} \cdot 2\text{H}_2\text{O}}$  ---- The corresponding  $[\text{Ca}_2\text{Al}(\text{OH})_6]\text{Cl} \cdot 2\text{H}_2\text{O}$  molar percentage deduced from the LCF analysis of chlorine molar percentage in  $[\text{Ca}_2\text{Al}(\text{OH})_6]\text{Cl} \cdot 2\text{H}_2\text{O}$  form among all the chlorine in fly ash

$m_{\text{Ca}, \text{Cl}, \text{F}}$  ---- The corresponding calcium molar percentage in



[Ca<sub>2</sub>Al(OH)<sub>6</sub>]Cl•2H<sub>2</sub>O form deduced from  $m_{[Ca_2Al(OH)_6]Cl \cdot 2H_2O}$

$m_{Al,Cl}$  ---- The corresponding aluminum molar percentage in

[Ca<sub>2</sub>Al(OH)<sub>6</sub>]Cl•2H<sub>2</sub>O form de-duced from  $m_{[Ca_2Al(OH)_6]Cl \cdot 2H_2O}$

$$m_{CaCl_2} = 50.5\% \div 2 = 25.3\% \Rightarrow m_{Ca,Cl,CaCl_2} = 25.3\% \quad (A-3)$$

$$m_{Ca,Cl} = m_{Ca,Cl,F} + m_{CaCl_2} = 49.2\% + 25.3\% = 74.5\% \quad (A-4)$$

$m_{CaCl_2}$  ---- The corresponding CaCl<sub>2</sub> molar percentage deduced from the LCF analysis of chlorine molar percentage in CaCl<sub>2</sub> form among all the chlorine in fly ash

$m_{Ca,Cl,CaCl_2}$  ---- The corresponding calcium molar percentage in CaCl<sub>2</sub> form deduced from  $m_{CaCl_2}$

$m_{Ca,Cl}$  ---- The corresponding calcium molar percentage in both CaCl<sub>2</sub> form and

[Ca<sub>2</sub>Al(OH)<sub>6</sub>]Cl•2H<sub>2</sub>O form deduced from  $m_{[Ca_2Al(OH)_6]Cl \cdot 2H_2O}$  and  $m_{CaCl_2}$

$$M_{Cl} = m_{Ca,Cl} + m_{Al,Cl} + m_{Na,Cl} + m_{K,Cl} = 74.5\% + 24.6\% + 15.3\% + 9.5\% = 123.9\% \quad (A-5)$$

$m_{Na,Cl}$  ---- The corresponding sodium molar percentage in NaCl form deduced from the LCF analysis of chlorine molar percentage in NaCl form among all the chlorine in fly ash

$m_{K,Cl}$  ---- The corresponding potassium molar percentage in KCl form deduced from the LCF analysis of chlorine molar percentage in KCl form among all the chlorine in fly ash

$M_{Cl}$  ---- The total metal molar percentage in all kinds of chlorides deduced from the LCF analysis of chlorines in fly ash

$$m_{Ca,Cl} : m_{Al,Cl} : m_{Na,Cl} : m_{K,Cl} = \frac{m_{Ca,Cl}}{M_{Cl}} : \frac{m_{Al,Cl}}{M_{Cl}} : \frac{m_{Na,Cl}}{M_{Cl}} : \frac{m_{K,Cl}}{M_{Cl}} = 60.1 : 19.8 : 12.3 : 7.7 \quad (A-6)$$

From table 1 the actual molar ratio of Ca, Al, Na and K in RFA can be calculated:

$$\left\{ \begin{array}{l} m_{Ca,P} = 24.7\% \div 40 = 0.6175\% \\ m_{Al,P} = 3.99\% \div 27 = 0.1478\% \\ m_{Na,P} = 2.97\% \div 23 = 0.1291\% \\ m_{K,P} = 2.99\% \div 39 = 0.0767\% \\ M_P = m_{Ca,P} + m_{Al,P} + m_{Na,P} + m_{K,P} = 0.9711\% \end{array} \right\} \quad (A-7)$$

$$m_{Ca,P} : m_{Al,P} : m_{Na,P} : m_{K,P} = \frac{m_{Ca,P}}{M_P} : \frac{m_{Al,P}}{M_P} : \frac{m_{Na,P}}{M_P} : \frac{m_{K,P}}{M_P} = 63.6 : 15.2 : 13.3 : 7.9 \quad (A-8)$$

$m_{Ca,P}$  ---- Molar amount of calcium in N gram fly ash

$m_{Al,P}$  ---- Molar amount of aluminum in N gram fly ash

$m_{Na,P}$  ---- Molar amount of sodium in N gram fly ash

$m_{K,P}$  ---- Molar amount of potassium in N gram fly ash

$M_P$  ---- Total molar amount of calcium, aluminum, sodium and potassium in N gram fly ash

### Appendix No.3

#### List of abbreviation

3R: Reduce, Reuse, Recycle

AES process: Acid Extraction-Sulfide Stabilization process

CaFA: fly ash collected in a bag filter with the injection of calcium hydroxide for acid gas removal

CEY: Conversion Electron Yield

CH: Calcium Hydrate

CSH: Calcium Silicate Hydrates

DTPA: Diethylenetriaminepentaacetate

EDTA: Ethylenediaminetetraacetate

FY: Fluorescence Yield

IEW: Ion Exchanged Water

LCF: Linear Combination Fit

L/S ratio: Liquid (ml) to solid (g) ratio

*MSW*: Municipal Solid Waste

*MSWI*: Municipal Solid Waste Incinerator

*NaFA*: fly ash collected in a bag filter with the injection of sodium bicarbonate for acid gas removal

*OPC*: Ordinary Portland Cement

*RFA*: Raw fly ash from the boiler or economizer of incinerator

*SCE*: Sequential Chemical Extraction

*S/S*: Stabilization/ Solidification

*TEY*: Total Electron Yield

*UCS*: Unconfined Compressive Strength

*UP*: Unsaturated Polyesters

*XANES*: X-ray Absorption Near Edge Structure

*XRD*: X-ray Diffraction

*XRF*: X-ray Fluorescence

# LIST OF MAJIOR PUBLICATIONS

## Journal Publications

- 1). Zhu F., Takaoka M., Shiota K., Oshita K., Kitajima Y. Chloride chemical form in various types of fly ash. *Environ. Sci. & Tech*, 2008, 42 (11), 3932-3937
- 2). Zhu F., Takaoka M., Oshita K., Takeda N.. Comparison of two kinds of fly ashes with different alkaline reagent in washing experiments. *Waste Management*, 2008
- 3). Zhu F., Takaoka M., Oshita K., Morisawa S., Tsuno H., Kitajima Y. Chloride behavior in washing experiments of two kinds of municipal solid waste incinerator fly ash with different alkaline reagents. *Journal of the Air & Waste Management Association*, accepted.
- 4). Zhu F., Takaoka M., Oshita K., Kitajima Y., Inada Y., Morisawa S., Tsuno H.. The study of chloride behavior in raw fly ash by X-ray absorption near edge structure and X-ray diffraction. *Analytical Sciences*, in review.

## International Conferences

- 1). Zhu F., Takaoka M., Oshita K., Matsumoto T., Takeda N., Tsuno H., Morisawa S.. The study of chemical form of chloride in raw fly ash. *The 13th Seminars of JSPS-MOE Core University Program on Urban Environment*, Beijing, China. 3 - 4 September, 2007
- 2). Zhu F., Takaoka M., Takeda N., Oshita K.. The influence of calcium hydroxide injection on washing process of fly ash. *Eleventh International Waste Management and Landfill Symposium*, S. Margherita di Pula, Sardinia, Italy, 1-5 October, 2007 (Copyright)
- 3). Zhu F., Takaoka M., Shiota K., Oshita K., Morisawa S., Kitajima Y. The sound material recycle of solid waste---the study on chloride chemical form in raw fly ash---. *9th APRU Doctoral Students Conference*, Far Eastern National University, Vladivostok, Russia, 14-18 July, 2008.